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ARPA Coupling Program on Stress-Corrosion Cracking

(Third Quarterly Report)

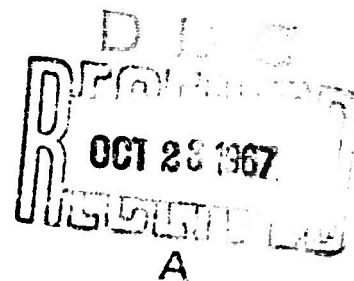
*nothing to be done
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Advanced Research Projects Agency
ARPA Order No. 878

25/938

August 1967



NAVAL RESEARCH LABORATORY
Washington, D.C.

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This research was supported by the Advanced Research Projects Agency of the Department of Defense, NRL Problem No. M04-08, and was monitored by the Naval Research Laboratory under Contracts Nos. Nonr-610(09), Nonr-760(31), and N00014-66-C0365.

ABSTRACT

A progress report of the research investigations being carried out on the problem of stress-corrosion cracking of high strength materials under ARPA Order 878 is presented. Work at Carnegie-Mellon University, Lehigh University, Georgia Institute of Technology, The Boeing Company, and the Naval Research Laboratory concerning physical metallurgy, surface chemistry, fracture mechanics, and characterization tests and translation related to stress-corrosion cracking is described. The materials being studied include high strength steels, titanium alloys, and aluminum alloys. Abstracts of recently published reports and a diary of events are included.

STATUS

This is a progress report; work is continuing.

AUTHORIZATION

NRL Problems 61M04-08
62M04-08
63M04-08A
63M04-08B
ARPA Order 878 and
RR 007-08-44-5512

INTRODUCTION

The increasing use of high-strength metals for complex and highly stressed structural applications has made the problem of stress-corrosion cracking (SCC) one of critical and immediate concern. Not only do corrosion cracks often grow more readily in materials of high tensile strength, but also the ability of such a material to contain a corrosion crack of a given size without catastrophic "brittle fracture" is much impaired compared with materials of lower strength (and higher toughness).

In order to learn how to improve high-strength structural alloys with respect to their resistance to SCC the Advanced Research Projects Agency of the Department of Defense has established under ARPA Order 878 a broadly based interdisciplinary attack upon the problem of SCC in high-strength titanium alloys, steels, and aluminum alloys. The project is composed of sectors located in The Boeing Company, Carnegie-Mellon University, Lehigh University, Georgia Institute of Technology, and the Naval Research Laboratory. In addition to having its own research activity, NRL has the responsibility for keeping the entire technical program attuned to DoD needs.

The complex phenomenon of SCC can be divided into four elements as follows: (1) the stress field, (2) the metallic phase, (3) the corrodent phase, and (4) the interface (with or without corrosion-product films) between metal and corrodent. Because of the obvious complexities of the phenomenon (and perhaps additional complexities not yet obvious), an interdisciplinary approach is essential.

The reporting system is as follows: Quarterly (commencing 1 January 1967) submissions from each unit of the project are submitted to section editors, who in turn submit the edited sections to NRL for publication as an NRL report. These sections must be kept brief to be manageable, and the project personnel are enjoined to publish the research details in the standard technical journals as a means of most effectively injecting the output of the program into the technological mainstream. When such publications are submitted to a technical journal, the abstract is included

in the quarterly report, so that interested readers may contact the author if the subject matter is of immediate interest. Additionally, the abstract will again be published in the quarterly report when the paper finally is printed in the technical journal and is presumably available in reprint form. Reprints or requests for advance copies of such papers (or advance information contained in the papers) should be addressed to the individual author or authors. Commencing with the Third Quarterly Report selected abstracts of reports and journal articles from outside the ARPA Program in the field of stress-corrosion cracking will be included as a service to readers of the Quarterly series.

The individuals responsible for directing this research at the various institutions and their participation as technical editors for the subject areas of their specialization in these progress reports are as follows:

Carnegie-Mellon University

H. W. Paxton, Project Director and Physical
Metallurgy Editor

Lehigh University

P. C. Paris, Project Director
A. C. Zettlemoyer, Director, Surface Chemistry Center,
and Surface Chemistry Editor

Georgia Institute of Technology

E. J. Scheibner, Principal Investigator, Surface
Chemistry
R. F. Hochman, Principal Investigator, Physical
Metallurgy

The Boeing Company

A. W. Bethune, Project Director
D. E. Piper, Alternate and Characterization Tests
and Translation Editor

Naval Research Laboratory

B. F. Brown, Program Director
E. P. Dahlberg, Assistant (General Editor)
R. A. Meussner, Deputy

A. PHYSICAL METALLURGY

It is well known that slight differences in heat treatment can markedly affect the stress-corrosion susceptibility of some alloys without significantly altering other properties. Similarly, slight composition or purity changes in high strength alloys may only have a predominant effect on the stress-corrosion resistance. The common aim of most of the physical metallurgy groups is thus to delineate which of the many possible metallurgical variables are important in any particular stage of the environmentally-induced sub-critical crack growth in any of the three most important types of high strength alloy. It is possible that a number of the projects will show two-fold benefits, firstly, in a method of improving the stress-corrosion resistance of the alloy being studied, and secondly in a greater understanding of the mechanism of the particular stress-corrosion process involved. Thus, although the experiments to date have largely been confined to materials of current engineering interest, it is by no means certain that this will continue to be so as the projects develop.

The majority of the physical metallurgy groups are situated in the university participants in the contract. It is, however, inherent in the nature of a university that its research programs require more time to build up momentum and become viable than those of a non-teaching research center; indeed, one of the stated aims of the contract is the involvement of students to an ever increasing extent. However, the stage has now been reached at all the universities concerned where the required new personnel have been attracted, sufficient student interest and involvement has been generated and considerable new equipment and apparatus has been purchased or designed and built. Thus, the year ahead should see the fruits of the first 12 months of the contract in the form of a greatly increased flow of useful data and results.

The following paragraphs describe the individual projects at all the participating institutes in each of the three main groups of high strength alloy, their current status, the results obtained and the probable future development.

STEELS

Carnegie Institute of Technology

A standard five-neck polarization cell is being used to determine potentiostatic anodic polarization curves for 18Ni maraging steel as a function of heat treatment. Dilute H_2SO_4 is being used to investigate the occurrence of passivation, and chloride additions are being made to this solution to investigate the disruptive effect of chloride ions. The polarization behavior in 3% NaCl will be determined during stress-corrosion cracking tests.

At this time experimentation is just beginning; the objective is to determine the capability of the system with respect to various techniques and the reproducibility of the resulting data. Preliminary results indicate that 18Ni maraging steel in the annealed condition will passivate in a dilute H_2SO_4 solution, but only to a very small extent.

The effect of impurities on the stress-corrosion susceptibility of the 18Ni maraging steel is being investigated. Sufficient high-purity melting stock to make 60lbs of maraging steel of nominal composition 18Ni - 9Co - 5Mo - 0.75 Ti - 0.075Al - Fe-balance with a total substitutional impurity content of considerably less than 50 p.p.m. has been purchased. From this material the P.D. Merica Research Labs of the International Nickel Company are currently preparing one 30lb. melt; the other 30lbs. of material are being held in reserve. From their own commercial purity melting stock, Inco are also preparing for this program 6 other 30 lb. melts of composition:

- (1) base alloy, same composition as high-purity melt
- (2) base alloy + 0.025% S
- (3) base alloy + 0.050% C
- (4) base alloy + 0.15 Si + 0.15% Mn
- (5) base alloy + 0.30% Cr
- (6) base alloy + 0.020% P

The resulting ingots will be hot-rolled by Inco to 3/8" x 9/8" bar, to be used as pre-cracked cantilever-beam specimens for stress-corrosion testing; a 3.5% NaCl environment will be used. The specimens will be heat-treated to a yield strength of about 275 k.s.i. The above procedure was adopted, in consultation with Inco, as smaller melts are liable to re-

sult in inhomogeneous specimens. The presence of the impurities in the commercially pure material should not mask the effect of the impurity addition. The selection of the above impurity additions was also made in consultation with Inco.

Dr. J. Y. Choi arrived at Carnegie Tech in March and work began seriously on this project then. A study of the advantages associated with using the analytical mass spectrometer for investigating the diffusion of hydrogen in steel in the vicinity of room temperature combined with the low cost of a small mass spectrometer, led to the purchase of such a unit (a so-called residual gas analyser). This and associated vacuum equipment should arrive in June. Auxiliary equipment that can be made here is now being built.

The next quarter will be spent in assembling the equipment, becoming familiar with it, and attempting to reproduce the data of Frank, Swets, and Fry¹ on the diffusion coefficient of hydrogen in iron at room temperature.

The effect of prior-austenite grain size on the environmentally induced sub-critical crack growth of AISI 4340 steel is being studied. Conventional heat treatments are being used to obtain a range of grain sizes varying from coarse to fine. In addition very fine to ultra-fine (A.S.T.M. 15) grain sizes will be developed, using a recently published repeated austenising and quenching technique.²

Currently, the specimens are being heat-treated to develop the requisite grain structures. After tempering at 400°F, which will result in a yield strength range of about 220 - 280 k.s.i., stress-corrosion testing will commence. Fatigue pre-cracked and side-grooved specimens, with a cross section of 1/2" x 3/2", stressed in cantilever bending with a 3.5% NaCl environment will be used.

¹ Frank R.C., Swets D.E. and Fry D.L., J. App. Phys., 29, (1958), 892.

² Grange R.A., A.S.M. Trans. Quart., 59, (1966), 26.

Georgia Institute of Technology

Evaluation of the stress-relieved properties of 316 and 316L has been completed. Figure A-1 shows the variation of the mechanical properties as a function of temperature for three hours heat treatment and figure A-2 provides an indication of the variation in mechanical properties as a function of heat-treatment time at 750°F. Corresponding to the increases of mechanical properties, up to 15% for the yield strength, marked increases in stress-corrosion cracking resistance, as measured by time to fracture, have been observed. The results indicate the initial increase in mechanical properties to be due to diffusion of carbon or nitrogen to dislocation sites locking dislocations. Preliminary electron microscopy studies indicate that the second increase may be due to a nickel-molybdenum precipitate. The initial increase in strength properties was also found in type 304 stainless steel, but the secondary hardening due to precipitation was not observed, indicating that the molybdenum in 316 and 316L is important for the secondary hardening effect.

Many studies have been performed on precipitates in austenitic stainless steel, but the temperature for stress-relief, this type of precipitate and the improved stress-corrosion resistance by this heat treatment have not been previously found. A review of the previous work on precipitates in austenitic stainless steel is summarized in references (1) through (12) (see list at end of section), and preliminary work on this stress relief treatment has been reported by Hochman and Taussig (13).

The Boeing Company

Five experimental 4340-type steels (compositions given in Second Quarterly Report) containing different amounts of silicon have been obtained. The influence of quenching and tempering at various temperatures within the range 400-1100°F on the tensile strength and pre-cracked Charpy values is currently being investigated. These data will be used to select the heat-treatment conditions necessary to achieve maximum tensile yield strength and a tensile yield strength of 200 ksi for each alloy. The stress-corrosion resistance of each alloy will then be evaluated at these two strength levels.

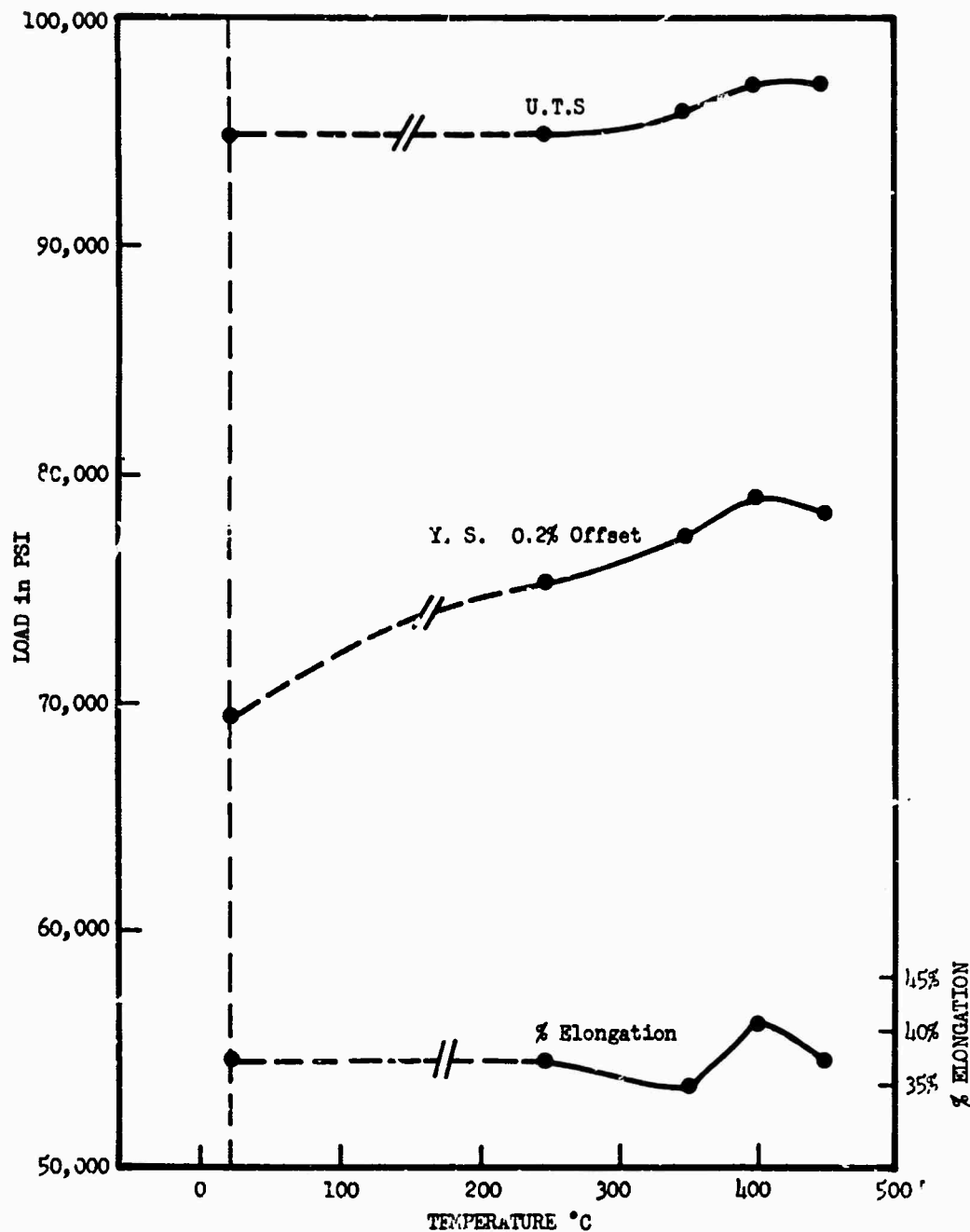


Figure A-1 - Variation of mechanical properties of quarter-hard 316L stainless steel as a function of 3 hours stress-relief at temperature.

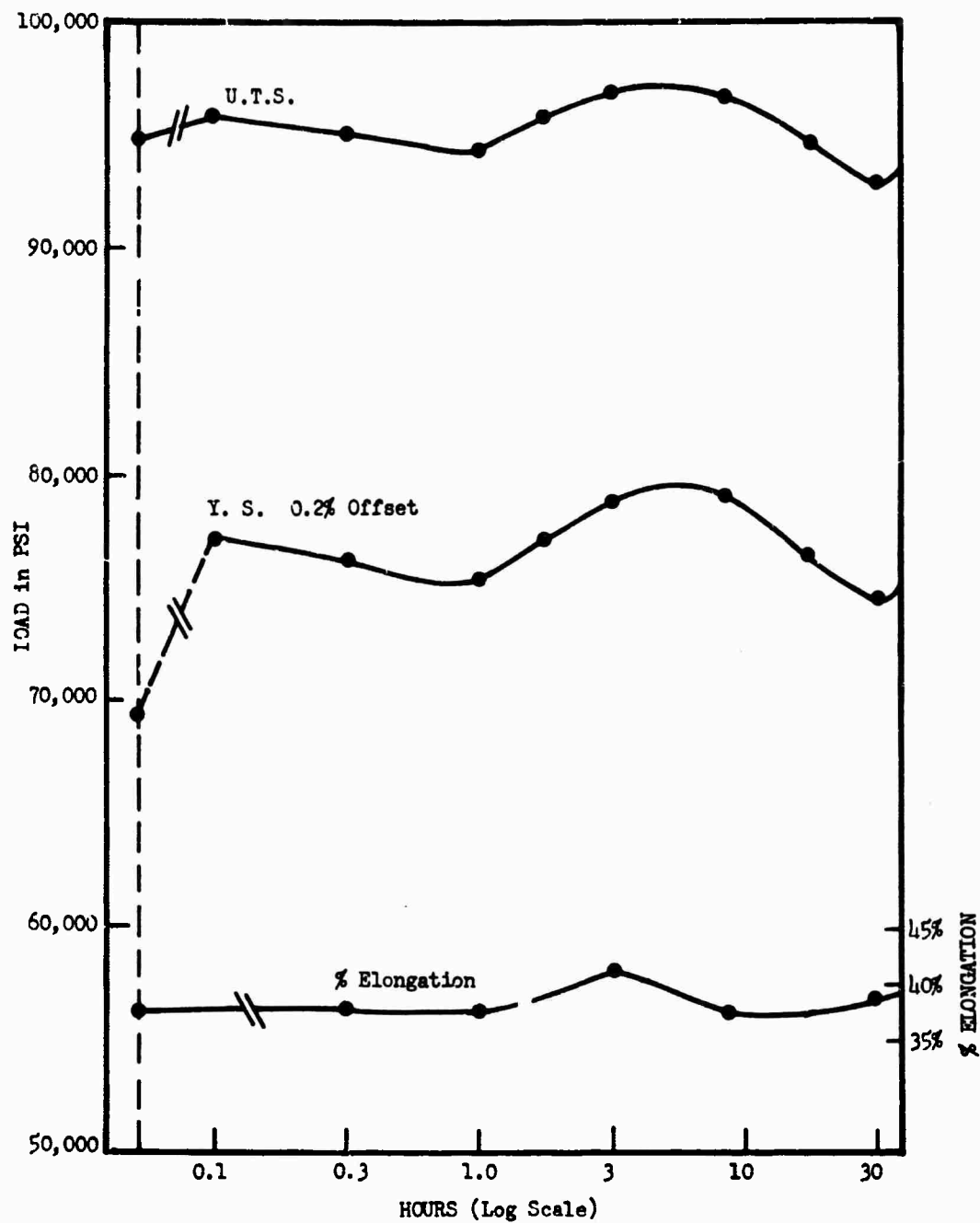


Figure A-2 - Mechanical properties of 316L stainless steel as a function of time at a stress-relief temperature of 750°F.

ALUMINUM ALLOYS

Carnegie Institute of Technology

The environmentally induced sub-critical crack-growth of the 7075 - T6 aluminum alloy in organic liquids is being studied. So far fatigue-precracked side-grooved specimens stressed in cantilever bending have been used; the specimen cross-section was $1/2" \times 3/2"$ and approx. 28,000 cycles were used to grow the fatigue crack to a length of about $1/4"$. The resultant crack was of the RW type.

To date two types of environment have been investigated, (a) various alcohols (methanol, "wet" and "dry" ethanol, ethylene glycol etc.), (b) ethanol with the addition of 1% of an halogen (bromine or iodine). With the alcohols, little crack growth in the W- direction occurred; however, there was considerable intergranular cracking in the R- direction, perpendicular to the original fatigue crack, as shown in fig. A-3. With the ethanol + 1% halogen environments, there was considerable environmentally induced, transgranular sub-critical crack growth in the W- direction and a number of fractures resulted; the initial plane-strain stress-intensity below which this does not occur is tentatively placed at about $0.4K_{Ic}$ for RW - type cracks. In unfractured specimens, the cracks were very wide and blunt and showed a tendency to branch intergranularly in the R - direction as shown in fig. A-4. In addition to this crack growth, there was some general corrosion, estimated at approximately 1 / hr.

Further testing rigs, to permit a study of WR cracks in 7075 - T6 in pure organic liquids using double-cantilever specimens, are currently being constructed. The growth of RW cracks or crevices in 7075 - T6 in ethanol + 1% halogen is being investigated further.

The stress-corrosion behavior of high purity Al-Zn, Al-Zn-Mg and Al-Cu alloys as a function of metallurgical structure is being investigated. In particular, attention will be focused on the precipitate distribution at and about the grain boundaries since it is in this vicinity that stress-corrosion failure occurs. By varying the size of the precipitate-free zone, it is hoped to elucidate the exact role of this region in the stress-corrosion behavior.



Figure A-3 - Intergranular R-direction stress-corrosion cracks originating from tip of transgranular W-direction crack; 7075- T6 exposed to methanol for 19,906 minutes at $K_{Ii} = 30.7 \text{ ksi } \sqrt{\text{in.}}$ 50X magnification.



Figure A-4 - Environmentally induced transgranular W-direction cracks showing some intergranular branching; 7075-T6 exposed to ethanol + 1% Br for 11,483 minutes at $K_{II} = 28.4$ ksi $\sqrt{\text{in}}$. 60X magnification.

Preliminary work on the Al-14.1% Zn sheets tested in the long transverse direction indicates that this alloy is susceptible to stress-corrosion cracking in 3.5% NaCl solution. Maximum susceptibility corresponds to the metallurgical condition obtaining just before peak hardness after isothermal aging at 155°C.

By employing double-cantilever geometry specimens of high-purity aluminum alloys, stress-corrosion crack length versus compliance during crack propagation will be measured. To supplement this mechanical study on polycrystalline aggregates, a strain-anneal technique is being perfected to obtain single- and bi-crystal specimens of the same alloys. These mechanical studies, combined with variations in heat-treating and aging conditions, should give related changes in the degree of corrosion susceptibility, and it is hoped to correlate the dependence of driving force on a crack resulting from the release of elastic energy during propagation to the crack velocity and micro-structure.

Preliminary results on polycrystalline specimens of Al- 15% Zn indicate a crack growth rate of 0.025 inches/hr. is obtained in 3% NaCl solution under fixed grip conditions with an initial value of K equal to 12 k.s.i. i.

Lehigh University

3 1/2% NaCl stress-corrosion cracking tests are being run on 7075 - T6 using 1/2" thick short-transverse cantilever specimens. The growth of the crack is being followed optically and with a L. V. D. T. Both methods of observation indicate uneven or discontinuous crack growth. Initial treatment of the crack growth rate data does not reveal a clear dependence between cracking kinetics and the stress intensity. Crack growth occurs at initial K_I values as low as 6,000 psi·in. and the ultimate failure occurs at K_I values around 15,000 psi·in. The initial fatigue crack profile (bowed) is altered to a nearly planar profile during the stress-corrosion cracking. The tests on 7075 - T6 are being continued to determine if a threshold K_I value exists below which cracking will not occur. In addition, the open circuit potential of the cracking specimen will be monitored to determine whether an electrochemical process is directly associated with the discontinuous cracking.

TITANIUM ALLOYS

Carnegie Institute of Technology

The possibility of removing oxygen from commercially pure titanium under high vacuum and temperature will be studied. A thermodynamic treatment of the process has suggested various approaches. The equipment for this experiment has been settled: measurements of electrical resistivity and mass spectrometer analysis will be performed to determine the effects of temperature, pressure and time on the process.

Samples obtained by the above method will be used to study the abnormal after-effect in this metal reported by Barrett* and the influence of the surface layer on the mechanical behavior of high purity titanium under different environments. At a later stage, studies will be carried out with titanium alloys.

The nature of the oxide film breakdown in titanium alloys will be studied by observing the onset of the abnormal after-effect in torsion specimens, and the nature of surface layer effects on shear deformation will be studied by looking at the effect of metal removal rate on torsion testing. A specific alloy system and a series of corrosion media will shortly be selected; the media under consideration at present are aqueous halide salt solutions.

Georgia Institute of Technology

Careful evaluation of the stress-corrosion cracking plane in the α phase in two large grain size titanium (7-2-1 and 8-1-1) alloys have shown a low angle relationship between the cleavage plane and the basal plane. Results of X-ray diffraction studies have indicated the average angle between the cleavage plane and the basal plane is approximately 14° . Fractographic work was performed on these surfaces and the typical cleavage type fracture observed verified the work at the NRL and the Boeing Company. A series of binary Ti-Al alloys of 3, 5, and 7 per cent aluminum are presently under study to provide more infor-

* Barrett C. S., Acta Met., 1, (1953), 2.

mation on the unusual crystallographic habit plane for stress-corrosion fracture in these alloys.

In the fractographic evaluation, the cleavage and river markings indicated rather large cleavage steps. Therefore the possibility of a series of small cleavage steps making up the variance between the basal plane and the plane of the fracture appears unlikely. In addition reflection from the fracture face indicates a smooth surface. With these considerations in mind several models have been considered for cleavage on an atomic scale. The importance of long range order in these systems was also considered. To date the most feasible explanation appears to be provided by a model of the ordered structure in Ti_3Al . A plane of approximately the correct index results when atomic steps occur where there is the highest concentration of titanium-aluminum bonds in ordered α . This is shown in figure A-5. These steps could not be observed by any variation in light reflection from the surface. Further studies are in progress; these include cutting sections from large grain size material for transmission electron microscopy. X-ray diffraction studies to obtain indications of the extent of long range ordering in these alloys are also underway.

With the field ion microscope system essentially complete, samples of titanium alloy wire which has been subjected to various heat treatments for stress-corrosion resistance and/or susceptibility will be examined by field ion microscopy. Dr. Brian Ralph, of the Department of Metallurgy in the University of Cambridge, England, will serve to aid in these studies during the summer as a visiting professor. A program on field ion microscopy is tentatively planned for late summer in conjunction with this project.

Studies are being initiated using line profiling analysis on single crystals to determine some of the basic considerations of surface oxide formation including epitaxy, crystallite size, strain effects, etc. This work is based on the techniques developed by Borie and Sparks* and will tend to bridge the gap between the fundamental surface studies and actual conditions.

* Borie B. and Sparks C.J., A Determination of Thin Oxide Film Thickness by Integrated Intensity Measurements, *Acta. Cryst.*, 14, (1961). 569.

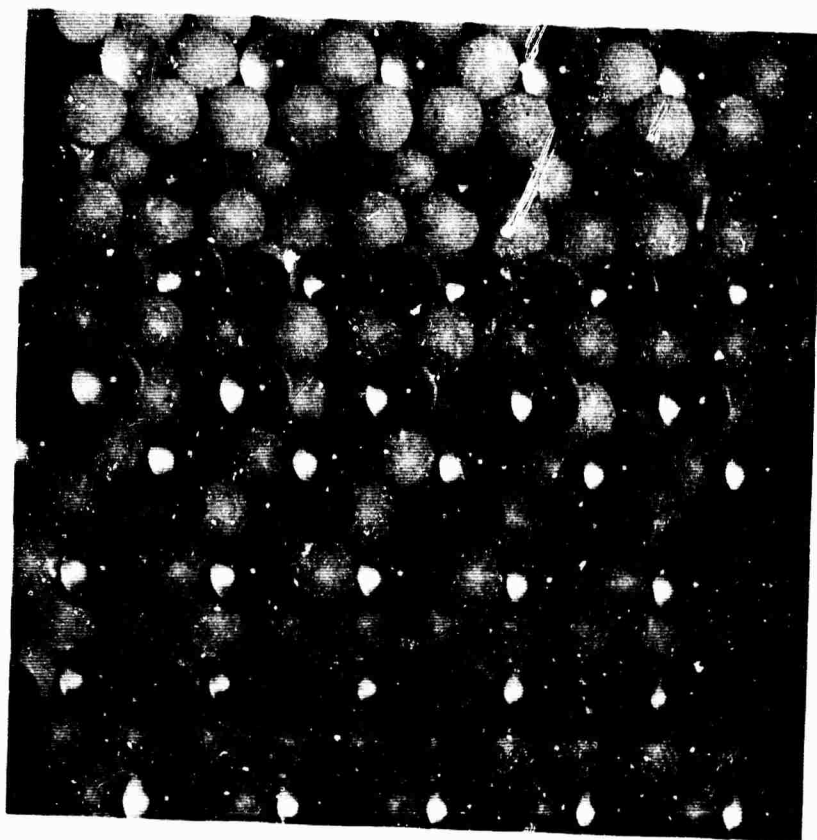


Figure A-5 - Ball model of the simulated fracture surface, with the aluminum atoms on the base plane designated by clear balls and on the matching plane, at the planar steps, by clear balls.

Lehigh University

Two heats of Ti - 6Al - 4V alloy have been received. One heat is mill annealed and 0.188" thick while the other has been hot rolled from 0.8" to 0.20" and is being ground to 0.188" thickness. The kinetics of the stress-corrosion cracking of these heats in an aqueous environment is being studied. The tests will be run on edge-notched specimens and the crack growth followed optically and by resistance methods. A gaseous environment chamber has been constructed so that the effect of relative humidity and temperature on the cracking kinetics can be studied.

The Boeing Company

The alpha phase in $\alpha + \beta$ titanium alloys has been shown to fail by cleavage in stress-corrosion tests but all the factors which contribute to this failure are not yet understood. For this reason, a study was made of commercially pure titanium (containing 0.38 wt% O_2 and 0.30 wt% Fe) which exhibited variations in stress-corrosion susceptibility as a function of heat-treatment condition (Table A-1). In this study, optical metallography, electron fractography and thin-foil electron microscopy were used to correlate microstructure with test results.

Table A-1: Heat-treatment conditions and SCC results

Heat-Treatment Condition	K_{IC} (ksi in.)	K_{ISCC} (ksi in.)
1500°F/30 min. /AC	111	94
1500°F/30 min. /WQ	116	41
1500°F/20 hr. /AC	106	42

The conclusions of this investigation were: -

- (a) Variations in stress-corrosion resistance as a function of heat treatment resulted from the transformation of the beta phase to $\beta + \omega_d$, $\beta + \omega$ and $\beta + \alpha$ (Omega phase which forms on quenching and causes diffuse reflections has been termed "diffuse ω " or ω_d by previous workers.)
- (b) As a result of the high oxygen content the alpha phase exhibited coplanar

slip.

- (c) The qualitative differences in stress-corrosion resistance were related to the ability of the transformed beta phase to nucleate a sharp crack. Crack propagation occurred when the alpha phase could not deform in a manner which would blunt the crack. Coplanar slip was related to this effect.
- (d) High iron and oxygen concentrations in combination could seriously degrade the stress-corrosion resistance of commercially pure titanium.

References:

- (1) Speich, G. R. and Clark, J. B., Precipitation from iron-base alloys proceedings of a symposium held in Cleveland, Ohio, October 21, 1963. New York 1965, Gordon and Breach Science Publ.
- (2) Cihal, V. and Jezek, J., Some observations on the nature of precipitating phases in 18/9/Nb steels. J.I.S.I. 202 (1964), 124-127.
- (3) Silcock, J. M. and Tunstall, W.J., Partial dislocations associated with NbC precipitation in austenitic stainless steels. Phil. Mag. 10 (1964), pg. 361.
- (4) Sumerling, R. and Nutting, J., Precipitation in 20% Cr - 25%Ni steel stabilized with niobium, J.I.S.I. 203 (1965), 390-395.
- (5) Irani, J.J. and Weiner, R.T. Aging behaviour of an austenitic steel containing vanadium, *ibid*, 913-921.
- (6) Hughes, H. Precipitation in alloy steels containing chromium, nickel, aluminum and titanium, *ibid*, 1019-1023.
- (7) Wilson, F.G. and Pickering, F.B., Effect of composition and constitution on the aging of austenitic steels containing aluminum and titanium, J.I.S.I. 204 (1966), 628-637.
- (8) Mazza, J.A. and Willoughby, G., Structural changes and creep mechanism in type 316 steel at 600°C, *ibid.*, 718-726.
- (9) Irani, J.J. and Dulieu, D., Precipitation in austenitic stainless steels containing tantalum, *ibid.*, 1229-1238.
- (10) Harding, H.J. and Honeycombe, R.W.K., Effect of stacking fault precipitation on the mechanical properties of austenitic

- steels., *ibid.*, 259-267.
- (11) Hopkin, L.M.T. and Taylor, L.H., Creep properties of Cr-Ni-Mo austenitic steel in relation to structure, *J.I.S.I.* 205 (1967), 17-27.
 - (12) Clark, B.R. and Pickering, E.B., Precipitation effects in austenitic stainless steels containing titanium and aluminum additions, *ibid.*, 70-84.
 - (13) Hochman, R.F. and Taussig, L.M., Improved properties of type 316L stainless steel implants by low-temperature stress relief, *J. of Mat.* 1, No. 2, 1966, 425-442.

B. SURFACE CHEMISTRY

ELECTROCHEMISTRY

The Boeing Company

Experiments on the anodic polarization of selected aluminum alloys are now in progress. Some passivation behavior around -0.700 volts (vs. S. C. E.) was exhibited by remelt 7075-T6 and by remelt 7075-T6 + 0.44 wt% Ag aluminum alloys. This passivation region was overlooked in earlier investigations because potential-step techniques were used. Further data will be collected before interpretations of results are attempted.

In the early stages of this program two commercially available cells were used; however, they are inconvenient to use, give poorly reproducible results, and are insufficiently versatile for the studies required. A new cell design, incorporating the best features of previous cells and adding many more, is now virtually complete.

Carnegie Institute of Technology

The experimental results reported here in terms of A (ohms) and B (milli-amperes⁻¹) were obtained from the empirical equation,

$$= A I / (1 + B I)$$

where E is the measured anode polarization voltage in millivolts and I is the current in milliamperes. Unless otherwise stated the anode surface area was 20 square centimeters, the temperature was 25° C, the electrolyte was water saturated with FeCl₂ (5.19 molar), and the atmosphere was hydrogen (1 atm.).

Alloys 4340 and 4140 were heated at 1550° F for one hour and then water quenched. Alloy RY was heated at 1430° F for one hour and oil quenched. The alloys showed Rockwell hardness of 55-65 on the C scale. The constants for the polarization equation are listed in Table B-1. The values in parentheses were obtained before heat treatment. Heat treatment improved the anode polarization of all alloys, especially that of the 4340 alloy.

Table B-1 - Constants for Polarization Equations

<u>Alloy</u>	<u>A (ohms)</u>	<u>B (milliamperes⁻¹)</u>
RY	131.3 (19.4)	2.0 (0.8)
4140	49.3 (12.7)	1.9 (0.4)
4340	24.0 (0.9)	-0.4 (0.5)

Two iron-manganese alloys were examined. Alloy 256 of 2.8% manganese gave for A, 103.9 ohms and for B 1.82 milliamperes⁻¹ while alloy 257 of 9.9% manganese gave for A, 70.4 ohms and for B, 4.08 milliamperes⁻¹. From these results

$$A = -4.72 (\% \text{Mn}) + 117.1$$

$$B = 0.32 (\% \text{Mn}) + 0.93$$

Thus, increasing the concentration of manganese decreases A. In contrast, alloy RY has more manganese (1.55% as opposed to 0.83% or 0.74%) than 4140 or 4340 alloys but also gives higher values for A. Further work should be done on, among other simple materials, iron-manganese alloys containing low percentages of manganese.

One iron-chrome alloy, number 138, containing 5.1 weight percent of chromium was available. It gave for A, 229.5 ohms and for B, 5.71 milliamperes⁻¹.

In all experiments a shielded iron reference electrode was used. Under normal procedures for measurement of polarization voltages the reference electrode is placed close to the outer surface of the anode, directly in the path of the current flow between anode and cathode. To measure any differences caused by the position of the electrode one iron reference electrode (termed inner) was placed inside the hollow anode. Iron wire, closely fitted inside a capillary tube with an open end dipping into the solution served as a second (outer) reference electrode. The outer reference electrode was in the path of the electrolyzing current, but protected by capillary tubing. For the inner electrode A was 115.0 ohms and B was 2.4 milliamperes⁻¹. For the outer electrode A and B were, respectively, 168.3 ohms and 2.5 milliamperes⁻¹.

The higher readings for the outer electrode are to be expected because a portion of the voltage recorded by the outer reference electrode is the IR drop through the electrolyte.

The kinetics of the anode polarization process are also of interest. The rate of this process increases with increased concentration of FeCl_2 and with increased electrolyzing current. With water solutions saturated with FeCl_2 a steady state is obtained, even at low currents (0.1 milliamperes), too rapidly for measurement. In the range 0.05 to 0.1 molar FeCl_2 , however, the voltage change obeys first order kinetics. The times to reach one-half of the final steady state voltage, $t_{1/2}$, are, for 0.1 molar FeCl_2 , about four seconds for a current of 0.1 milliamperes and 0.6 seconds for a current of 1.0 milliamperes. Added NaCl appears to speed up the rate slightly while added CaCl_2 (0.9 molar) slows down the rate approximately by a factor of 30. These experiments are being made with Armco ingot iron electrodes and their precision at present is about $\pm 15\%$.

Naval Research Laboratory

A high-purity closed electrochemical system for an investigation of passive iron has been constructed. Potentiostatic measurements in helium-saturated sodium hydroxide solutions have shown that the entire passive region is subdivided into several regions, each with a different slope for the potential vs. log current density plot. The different slopes can be interpreted in terms of conducting and nonconducting films. All of the passive films are so thin that they are invisible, and the appearance of the wire does not change with increasing potential. Work planned should assist in elucidating the influence of the passive films on the electrode processes occurring at the iron-solution interface at different electrostatic potentials.

LEED AND ELECTRON EMISSION

Georgia Institute of Technology

To investigate from an atomic point of view the oxidation of aluminum, titanium, and 25-18 stainless steel, low energy electron diffraction and low energy electron spectroscopy studies have been begun. In most cases the specimens are prepared by acid sawing, acid polishing, and electro-polishing techniques which were developed particularly for the present LEED

investigations. Ion bombardment and high temperature annealing are also used to further treat the samples before the spectra are taken and aluminum is rf sputtered to remove the oxide layer before the sample is mounted in the diffraction unit.

Although low energy electron diffraction is capable of determining structural changes which occur in the first layers of a solid upon oxidation, considerable ambiguity remains in these determinations when the oxidation reaction does not result in known bulk structures. The diffraction patterns can be used effectively in any case to determine definite stages of the surface reaction. The characteristic loss and the secondary electron portions of the low energy electron spectroscopy curves yield information concerning the electronic nature of the adsorbate-substrate interactions as has already been demonstrated in extensive Auger electron energy distribution studies of tungsten and copper done in other laboratories.

The present work with aluminum has not proceeded past attempts to obtain an atomically clean surface. Figure B-1 shows the diffraction pattern and energy distribution curve from an aluminum (111) surface. The diffraction pattern shows the spacing and symmetry that would be predicted for the atomic arrangement of the (111) plane of a fcc structure, but even extensive ion bombardment and high temperature annealing has failed to produce background-free diffraction patterns. Similarly, the secondary electron energy distribution shows a subsidiary peak that is not expected for a clean surface. At temperatures near the melting point considerable evolution of argon was noted with a residual gas analyzer. The latter observation, combined with the LEED and electron spectroscopy results, indicates that with the ion energies required to remove the oxide and other impurities, the resulting damage and argon occlusion do not allow the formation of the desired surfaces. It may be necessary to provide for rf sputtering within the diffraction chamber. These investigations will later be extended to include titanium and stainless steel.

MACROSCOPIC SURFACE MEASUREMENTS

Lehigh University

Investigations into the variation of the surface activity of iron-chrome alloys

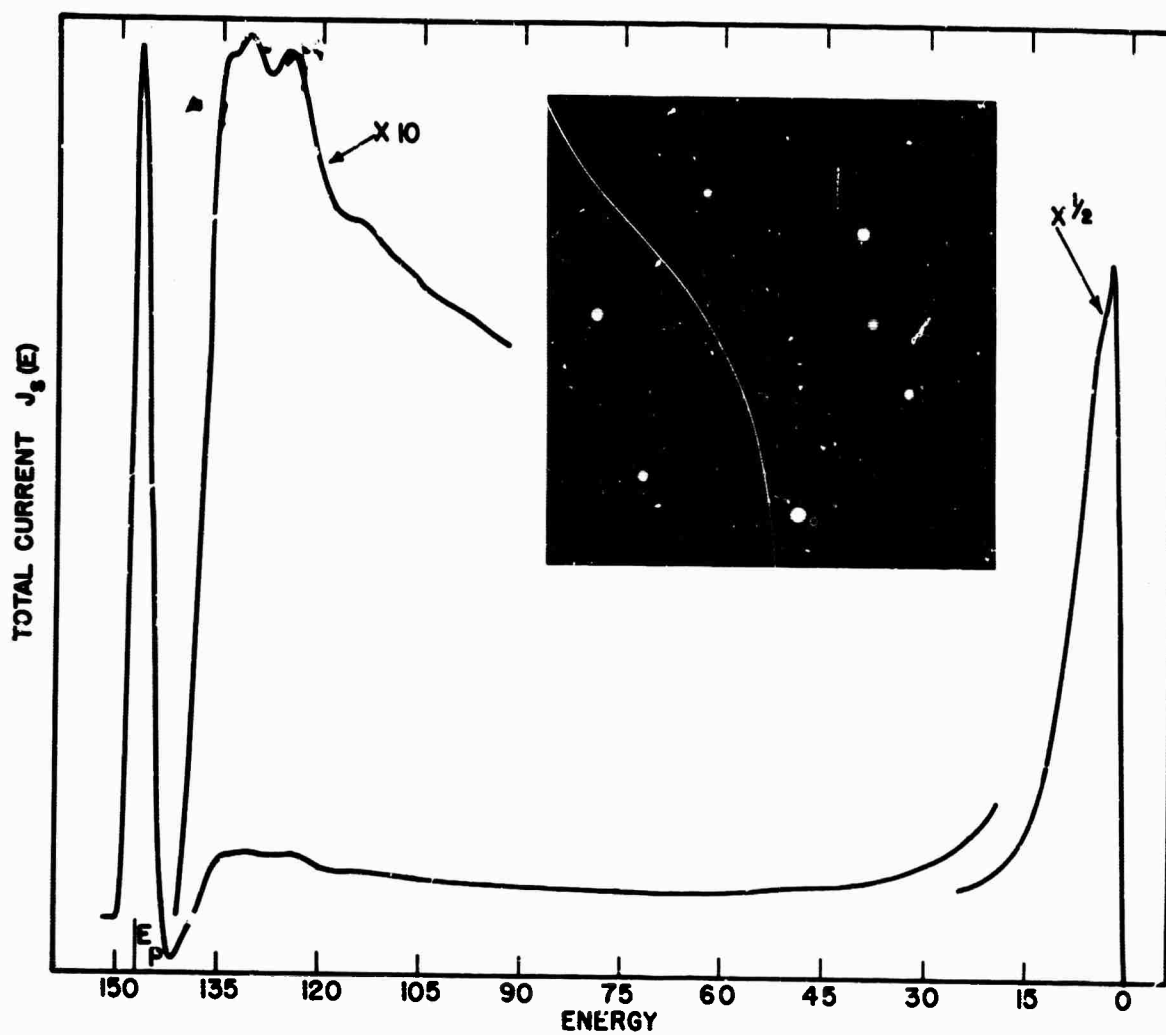


Figure B-1 - LEED pattern and energy distribution curve from an aluminum (111) surface.

in the decomposition of nitrous oxide as a function of the percent chromium at the surface of the alloy are continuing. Oxidation of the wire occurs during the decomposition and nitrogen is the only product, although there are some indications that the dissolution of oxygen in the wire becomes more difficult as the oxide layer builds up during an experiment. Carbon has unfortunately appeared as a contaminant in the system; however, this experimental difficulty will probably soon be resolved, and further quantitative information concerning the relationship between chromium content and passivation is anticipated.

Studies of the adsorption of anhydrous HCl on iron and some of its alloys can be expected to yield information concerning the passivation and SCC of materials in a saline water environment. "Clean" iron can be expected to chemisorb HCl through the chlorine end of the molecule, and at higher temperatures FeCl_2 and H_2 could be produced. The presence of an oxide coating on the surface could change the mechanism of adsorption to one of adsorption at oxygen sites through the hydrogen end of the HCl molecule; consequently, the influence of presorbed oxygen on the adsorption of HCl is also of interest. Preliminary experiments reveal that HCl adsorption does occur on iron and can be observed with an Orr type apparatus using Aplezon-B oil in the manometer. The Langmuir adsorption appears to be complete at very low relative pressures.

In consideration of the current interest in the stress corrosion of titanium alloys, flash desorption techniques are being applied to investigations of the interactions of hydrogen with titanium instead of with the iron-chrome alloys mentioned earlier. The absorption of hydrogen by titanium may cause difficulties; nevertheless, much meaningful information can be obtained from such a study. Calibration of gauges, valves, etc. using a tungsten filament and high purity hydrogen gas is now in progress.

By far the most productive phase of surface chemistry research at Lehigh University in connection with stress-corrosion cracking has been the E. P. R. work. The rate of stress-corrosion-cracking of titanium and its alloys is known to be a function of oxygen and dinitrogen tetroxide concentrations in the environment, and surface effects probably play an important role in the SCC mechanism. Real surfaces of titanium are coated with an oxide layer under atmospheric conditions, and qualitative studies are presently being made on low area rutile (TiO_2) under various gaseous environments.

The E.P.R. spectra of low area rutile are significantly different from those of high area rutile. Although after vacuum outgassing a singlet attributed to Ti^{+3} is observed in spectra of both low and high area rutile, after treatment with oxygen two triplets, observed with high area rutile centered around $g = 2.002$ and attributed to O_2^+ , are absent with low area rutile. A signal identified with surface O_2^- on low area rutile is clearly a triplet, whereas the same signal is partially masked by the O_2^+ signal with high area samples. Treatment of TiO_2 rich in Ti^{+3} with nitrogen dioxide results in oxidation of Ti^{+3} but no O_2^- signal is observed.

The presence of hydrogen trapped between oxygen atoms in the bulk of TiO_2 single crystals grown by the Verneuil method has been shown by IR studies and slow neutron inelastic scattering measurements. The interaction of hydrogen with Ti^{+4} ions can lead to formation and stabilization of Ti^{+3} ions, but the Ti^{+3} ions produced during vacuum outgassing are not subject to any stabilizing influence. Attempts are now being made to distinguish between the two types of Ti^{+3} species by spin resonance studies of their interactions with, among other gases, oxygen at room temperature.

Several investigators have studied the influence of hydrogen, nitrogen, and oxygen chemisorption on the ferromagnetic resonance of small particles (10 to 100 Å.) of nickel in supported nickel catalysts. An attempt will be made to extend these studies of gas adsorption on small particles to an investigation of gas adsorption on nickel and iron thin films (100 to 600 Å.), wires or whisker crystals. Such specimens can be stressed so that preferential chemisorption of gases on stressed surfaces can be studied. Information concerning the reaction of water at crack tips can possibly be obtained. Evidence will be sought either for the stress sorption cracking mechanism, or for the hydrogen embrittlement mechanism for stress-corrosion cracking.

Naval Research Laboratory

As part of the program of the Chemistry Division on corrosion related directly to and supported by the ARPA Coupling Program radioactive tracers have been used to study metallic surfaces with respect to the arrangement, type, and concentration of active adsorption sites. A linear relationship was demonstrated between the radioactivity of and the

methylene iodide contact angle on iron and glass surfaces covered by an adsorbed film of radioactive stearic acid. If equivalent films (monolayers) of stearic acid are deposited on both iron and fire-polished soft glass (the chosen reference standard of unit roughness) the greater radioactivity of iron compared to glass gives a direct measure of the surface roughness of the iron. The rates of decrease of radioactivity with heating, solvent treatment, or exchange with inactive stearic acid in solution indicate that approximately 60% of a compact stearic acid monolayer is rather weakly bonded to iron while 40% is more strongly, probably chemically, bonded. NRL Report #6553, entitled "The Adsorption of C-14 Labeled Stearic Acid on Iron" is scheduled for publication in June.

Currently in progress are studies of the effects of concentration on film formation and the effects of temperature on desorption rates. Highly polished samples of Armco iron, high purity nickel, chromium, types 304 and 416 stainless steels, and high tensile steels are being prepared for adsorption-desorption studies which should better define the reaction of the metallic surface with radioactive stearic acid, hexadecylamine, or other reactive molecules.

Studies are also being made of oxide films formed on ferrous metals and alloys in aqueous media. A review of the literature has revealed that the protective films are usually spinel-type oxides in which the Fe_3O_4 arrangement may be modified by vacancies and by hydrogen or some other cation replacing some of the ferrous ions in the oxide. Protective films generated on 18-8 stainless steel by exposure to hot water were spinels containing nickel and chromium in approximately the proportions of the parent metal; however, prolonged exposure to hot water effected a chromium and nickel enrichment which tended to make the films insoluble in acid.

The presence of cobalt in spinel films evidently confers some resistance to acid and chloride attack, and the incorporation of lithium into protective spinel films evidently conveys resistance to attack by hot water and some immunity to breakdown by oxygenated aqueous chloride solutions. In addition, some of the molybdenum and silicon in type 316 stainless steel is incorporated in the protective films and imparts improved resistance to chloride breakdown. Water is present in those films on stainless steel which are produced by passivating treatments and give maximum resistance

to pitting in chloride solutions. The hydrogen in the latter films is tightly bound in the structure; its removal is accompanied by substantial loss of protective properties. Further studies of the relationships between film composition and resistance to chemical attack are under way.

C. CHARACTERIZATION TESTS AND TRANSLATION

TEST TECHNIQUES AND PROCEDURES

The goals of the characterization and translation study have been consolidated during the past year. Before the extensive testing of high-strength alloys was undertaken, it was necessary to prove that the stress-corrosion cracking (SCC) phenomena were related to stress intensity. Wedge-force-loaded panels were prepared at Boeing from Ti-8Al-1Mo-1V sheet (0.160 in. thick) and tested in a 3.5-percent NaCl solution. The dependence of SCC on stress intensity was demonstrated convincingly for this alloy (see Abstracts of Published Reports: "A Study of Stress-Corrosion Cracking by Wedge-Force Loading," H. R. Smith, D. E. Piper, and F. K. Downey). Brown and Beachem* at NRL demonstrated that $K_{I_{SCC}}$ was an intrinsic material property when they obtained the same $K_{I_{SCC}}$ values on three different specimen configurations (center-cracked and surface-flawed tension specimens and cantilever bend specimens) of a 4340 steel. Preliminary crack growth rate data generated at Boeing on 7075-T651 and 2024-T3 aluminum alloys and on mill-annealed Ti-6Al-4V in air and in 3.5-percent NaCl solution show that the stress-intensity factor approach can be used to correlate fatigue crack growth rate data in corrosive environments for these alloys. This was demonstrated by the agreement in crack growth rates of wedge-force-loaded and center-cracked panels tested at the same stress-intensity factor. Further studies are planned at Boeing to evaluate an aluminum alloy by wedge-force loading in 3.5-percent NaCl solution and a titanium alloy by wedge-force loading in a corrosive organic environment.

Collation of test results from Boeing and NRL was reported in the ARPA Second Quarterly Report (p. 26). It was concluded that neither the difference in stressing method (four-point bending at Boeing versus cantilever bending at NRL) nor the sequence of addition of solution affected the determination of $K_{I_{SCC}}$ for mill-annealed Ti-8Al-1Mo-1V plate. Tests on Ti-4Al-3Mo-1V plate for which the order of solution and load application was reversed were conducted at Boeing and no effect on $K_{I_{SCC}}$ was observed. This further substantiated the conclusion that the order of salt-load application does not affect $K_{I_{SCC}}$, since no effect was observed in either the susceptible Ti-8Al-1Mo-1V or the relatively immune Ti-4Al-3Mo-1V alloy. It was recognized that the elapsed time between loading the specimen and adding the aqueous environment might affect SCC susceptibility. Since any effect might depend on the creep

*B. F. Brown and C. D. Beachem, "A Comparison of Three Specimens for Evaluating the Susceptibility of High-Strength Steel to Stress-Corrosion Cracking," internal report, Naval Research Laboratories, 1966.

characteristics of the particular alloy, it has been recommended that the environment be added prior to load application during SCC characterization testing. The similar $K_{I_{SCC}}$ values for different specimens of 4340 steel,* including the cantilever bend specimen, indicate that satisfactory comparisons may be obtained on at least four precracked specimen configurations.

Additional large tension specimens (1 in. by 6 in. by 24 in.) containing surface thumbnail flaws are being prepared at NRL to further demonstrate the direct correlation between the results obtained in tension tests and cantilever-beam tests with respect to the crack-tip stress intensity for the initiation of slow crack growth in sea water. Slow crack growth was observed to begin at a K_I level of $31 \text{ ksi}\sqrt{\text{in.}}$ for a Ti-7Al-2Cb-1Ta alloy in both the tension and bend test specimen configurations (see ARPA Second Quarterly Report, p. 27). Tension test specimens of this alloy with various initial flaw sizes are being prepared. Specimens of a Ti-6Al-4V alloy with a high $K_{I_{SCC}}$ will soon be tested. Although these large-scale tests are expensive and difficult to conduct, they provide the information that demonstrates the validity of translating cantilever-bend test results to engineering structures.

Studies are continuing toward improving existing quantitative test techniques for SCC. During the past year, NRL has experimented with several different SCC test specimen configurations and testing procedures in attempting to develop a constant K_I level test and/or a single-specimen test for determining $K_{I_{SCC}}$. Initial tests were carried out on a novel "double bend" configuration specimen** that provided a constant K_I over an extensive range of crack sizes. These tests were not successful because the crack front did not remain perpendicular to the specimen surface, which made growth rate measurements difficult. Tapered specimens of Ti-7Al-2Cb-1Ta are now being prepared for double-cantilever-beam tests. Past attempts by some individuals to use this specimen have been unsuccessful because of the tendency for the crack to propagate away from the symmetry plane. The specimens now being prepared will be 1 in. thick and will contain shallow, rounded side grooves to help contain the crack in the desired plane. Crack arrest tests with the cantilever-beam apparatus are being developed at the NRL Marine Corrosion Research Laboratory at Key West, Florida. This test apparatus will be instrumented so that a fixed amount of the load will be removed from the specimen as the crack grows. The hope is that the $K_{I_{SCC}}$ level can be reached conveniently with a single specimen.

*B. F. Brown and C. D. Beachem, previously cited.

**J. O. Outwater and P. J. Gerry, "On the Fracture Energy of Glass," University of Vermont, Contract NONR 3219(01)(x), August 1966.

Modification of existing SCC test techniques at Boeing includes the use of dynamic bend testing to determine K_{ISCC} . Single-edge-cracked specimens were four-point bend tested in a 3.5-percent NaCl solution and the load-deflection curves were autographically recorded to determine whether the stress-intensity value at deviation from linearity coincided with the known K_{ISCC} value for the material. The loading rates during the tests were kept low to allow the SCC to proceed. Preliminary data are shown in Table C-1.

Table C-1
Results of Dynamic Bend Testing in 3.5-Percent NaCl Solution

Alloy	K_{IC} (ksi $\sqrt{\text{in.}}$)	K_{ISCC} (Static) (ksi $\sqrt{\text{in.}}$)	K_{ISCC} (Dynamic) (ksi $\sqrt{\text{in.}}$)	Load Rate (lb/min)
Ti-8Al-1Mo-1V (Mill Annealed)	48	20	24	300
			28	1,440
Ti-4Al-3Mo-1V (β -STA 1250)	95	70	70	300
			65	1,440
4330 (V-Modified)	100	40	92	300
			80	300

The results indicate that the test could be advantageous as a screening technique for titanium alloys, since it involves the testing of only one specimen over a short period of time. However, the technique is not satisfactory as a method of determining the stress-corrosion resistance of steels.

Increased efforts will be made at NRL and Boeing to recommend a procedure for evaluating the stress-corrosion susceptibility of precracked specimens of high-strength steels and titanium and aluminum alloys. The necessary experiments will be performed to justify these recommendations, and the associated terminology and methods of cataloging data will be scrutinized.

GENERAL CHARACTERIZATION STUDIES

Concurrent with the studies of test techniques and stress intensity — SCC relationships, high-strength alloys have been characterized by both NRL and Boeing during the past year. The overall objective of this testing is the development of high-strength alloys that are resistant to SCC.

SCC in Salt Solution

A collection of all the SCC data on titanium alloy base plates and weldments has been submitted for publication as a formal NRL report. The report, "Stress Corrosion Cracking of Alloys of Titanium in Salt Water," NRL Report 6564, by R. W. Judy, Jr. and R. J. Goode, was compiled to aid those concerned with material selection, with studies of the mechanism of SCC in titanium alloys, and with alloy development (see Abstracts of Published Reports).

Initial studies have been conducted at Boeing on two alpha-type alloys: commercially pure titanium ($O_2 = 3,800$ ppm) and Ti-5Al-5Sn-5Zr. The commercially pure alloy was tested in nine thermal conditions. Specimens in a $1500^\circ\text{F}/30$ min/WQ condition and a $1500^\circ\text{F}/20$ hr/AC condition were susceptible to SCC. Fractographic analysis of specimens given these heat treatments showed the fracture mode to be particularly sensitive to grain orientation. In the stress-corrosion region, approximately half of the alpha grains failed by cleavage, whereas the rest failed by ductile tearing. Thin-foil studies have attributed the SCC susceptibility of specimens in the water-quenched condition to precipitation of omega in the beta phase (see Physical Metallurgy section). Stabilizing at 1050°F raised the stress-corrosion resistance of these specimens to the level of annealed specimens by transforming brittle omega to alpha. Quenching from 1700°F transformed beta to martensite, rather than omega, and resulted in immunity to SCC.

The SCC susceptibility of specimens in the $1500^\circ\text{F}/20$ hr/AC condition illustrates the importance of grain size on SCC. This treatment increased the average alpha grain diameter 40 percent over the grain size produced by the $1500^\circ\text{F}/30$ min/AC heat treatment, but reduced K_{IC} , K_{ISCC} , and the susceptibility ratio, K_{ISCC}/K_K , from 0.84 to 0.35. The 0.2 percent yield strength also decreased. This behavior is consistent with dislocation theories of yield and of fracture and suggests that sensitivity to environment increases with grain size. Recovery, as well as recrystallization and grain growth, are also being studied in material annealed at various temperatures after 30 percent reduction by cold rolling. Initial results show that recovery produced by a $925^\circ\text{F}/20$ min/AC treatment increases susceptibility to SCC.

Addition of elements such as aluminum, tin, and zirconium to strengthen and stabilize the alpha phase increased susceptibility to SCC, as measured by the susceptibility ratio. The susceptibility ratios of the following alloys in the annealed condition were 0.83 for commercially pure titanium, 0.65 for Ti-5Al-5Sn-5Zr, 0.5 for Ti-5Al-2.5Sn, and 0.5 for TX684 (Ti-6Al-5Zr-1W-0.2Si). Stabilizing the Ti-5Al-5Sn-5Zr alloy after a high-temperature

treatment further reduced resistance to SCC, whereas water quenching from 1650°F increased it. Changes in the deformation characteristics of alpha caused by ordering have been correlated with this behavior.

Beta-stabilizing additions generally improved the stress-corrosion resistance of alpha-beta type alloys. Earlier work has shown that beta particles in Ti-6Al-4V and Ti-4Al-3Mo-1V arrested stress-corrosion cracks that propagated readily through equiaxed alpha grains. A series of ternary alloys, Ti-7Al-2.5Mo, Ti-7Al-3Mo, and Ti-7Al-4Mo, is being analyzed to relate volume percent beta to SCC. Preliminary studies have shown that K_{ISCC}/K_{IC} is 0.58 for annealed Ti-6Al-2Mo, 0.67 for annealed Ti-7Al-4Mo, 0.8 for annealed Ti-5Al-3Mo-2Sn, and 0.6 for the standard composition of Ti-6Al-6V-2Sn (containing 0.7 Fe and 0.7 Cu). The size and distribution of beta particles, as well as the type and amount of element added, combine to control susceptibility. The presence of intermetallic formers such as iron, copper, and silicon is particularly critical. Hylite 50 (Ti-4Al-4Mo-2Sn-0.5Si), an alloy similar to Ti-4Al-3Mo-1V and Ti-5Al-3Mo-1V-2Sn except that it contains silicon, is considerably more susceptible than either alloy.

The fracture toughness, stress-corrosion resistance, and susceptibility ratio of several annealed alloys may be seen in Fig. C-1. The corresponding ultimate tensile strengths are shown in parentheses. In general, commercially pure titanium and alloys containing low aluminum and high beta isomorphous stabilizers are the toughest and most resistant to SCC.

The studies on the effects of environmental heat-treating conditions on the SCC resistance of titanium alloys are being continued at NRL.

A Ti-7Al-1Mo-1V alloy was susceptible to SCC in the as-received condition. Cantilever bend specimens of this alloy were vacuum solution annealed at 1950° and 1700°F (above and below the beta transus respectively) for 1 hr and cooled in purified helium. The 1950°F heat treatment resulted in a coarse-grained microstructure that is characteristic of this material when it is heat treated above the beta transus. Similar specimens, which were given a 1700°F vacuum solution anneal for 1 hr, retained their original fine-grained microstructure. Both the vacuum solution annealing heat treatments rendered the material immune to SCC in a 3.5-percent NaCl solution. The K_{ISCC} value of 112 ksi√in. for this alloy in the WT fracture direction was obtained by step loading from a stress intensity of 101 ksi√in., a value that had been maintained for 60 min without evidence of SCC. However, a heat treatment similar to the 1700°F vacuum anneal, but in an argon atmosphere followed by air cooling, did not eliminate the SCC sensitivity of this alloy. Specimens given that heat treatment failed in the 3.5-percent NaCl solution at a stress

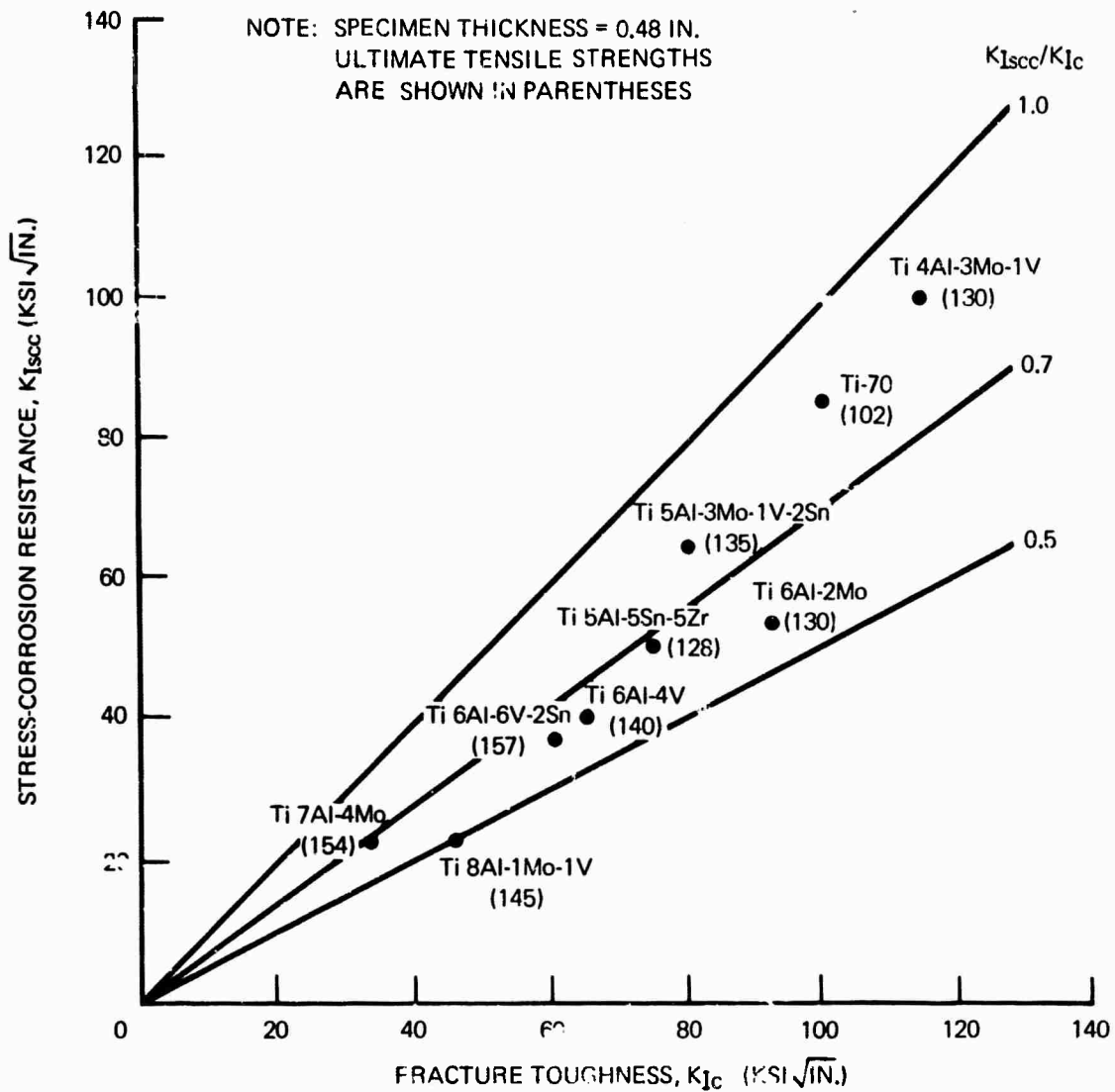


Figure C-1 - Stress-corrosion resistance of mil' - annealed titanium alloys in 3.5-percent NaCl solution.

intensity of 64 to 68 ksi $\sqrt{\text{in.}}$ in 1/2 to 1-1/2 min. The actual $K_{I\text{SCC}}$ threshold value for the material has not been established, but it will be somewhere below that level of stress intensity. The hydrogen contents of the Ti-7Al-1Mo-1V material in the conditions described above were:

As-received	60 ppm hydrogen by wt
1950°F vacuum heat treatment, helium cooled	7 to 8 ppm hydrogen by wt
1700°F vacuum heat treatment, helium cooled	19 to 23 ppm hydrogen by wt
1700°F argon heat treatment, air cooled	38 to 46 ppm hydrogen by wt

A study was conducted to determine the effect of cooling rate on the SCC susceptibility of the Ti-7Al-1Mo-1V alloy. Specimens that were vacuum solution annealed at 1700°F were either furnace cooled in vacuum or cooled at a much faster rate by purging the vacuum chamber with purified helium gas at room temperature. The specimens were cooled at an average rate of 32.1° and 52.3°F/min (over a 20-min period) in the furnace under vacuum and helium respectively. In both cases, the specimens were not susceptible to SCC in a 3.5-percent NaCl solution. Specimens solution annealed at the same temperature for the same length of time in argon or helium atmospheres and furnace cooled at the intermediate average cooling rates of 43.1° and 49.3°F/min respectively were susceptible to SCC under identical test conditions. These cooling rates are intermediate to the two employed after the vacuum solution annealing treatments. The results show that for this Ti-7Al-1Mo-1V alloy and the rather limited range of cooling rates studied, the rate of cooling was not a primary factor in SCC susceptibility. Rather, the environmental conditions associated with the solution annealing treatment appeared to be the major factor.

Studies were also conducted to determine whether the beneficial effects produced by the vacuum solution annealing heat treatments were permanent or whether a temporary immunity to SCC existed. Results of these SCC tests show that 9 months after the vacuum solution annealing, the Ti-6Al-4V, Ti-7Al-1Mo-1V, and Ti-7Al-2.5Mo alloys all had $K_{I\text{SCC}}$ values of over 100 ksi $\sqrt{\text{in.}}$ and still had no visible evidence of SCC attack on the fracture surfaces of the specimens tested in a 3.5-percent NaCl solution.

The benefits of vacuum solution annealing on SCC resistance shown in earlier studies on Ti-8Al-1Mo-1V, Ti-7Al-1Mo-1V, Ti-6Al-4V, and Ti-7Al-2.5Mo alloys have also been established for a Ti-6Al-6V-2.5Sn alloy having an

as-received K_{ISCC} of 34 ksi $\sqrt{\text{in.}}$. In particular, after a 1650°F vacuum solution anneal followed by helium cooling, the material withstood an applied stress intensity of over 120 ksi $\sqrt{\text{in.}}$ for over 20 hr in a 3.5-percent NaCl solution. The K_{ISCC} value, reproducibly obtained, was 124 ksi $\sqrt{\text{in.}}$ for the RT fracture direction and 134 ksi $\sqrt{\text{in.}}$ for the WT fracture direction. These values are the same as the K_{IX} (dry break in air) value for this alloy. A 1550°F solution anneal in an argon atmosphere followed by water quenching produced a condition where the K_{ISCC} value was 21 ksi $\sqrt{\text{in.}}$. The two solution annealing temperatures indicated are below the beta transus (1735°F) for this alloy.

SCC in Organic Liquids

In the course of studies at NRL of the effects of organic environments on the SCC of titanium alloys, it was found that some titanium alloys display delayed fractures at K levels considerably lower than K_{IC} or K_{IX} , even in a dry air or dry helium environment. A threshold value for these conditions was found and designated K_{IH} . This threshold was found to increase as the specimen width was decreased below the critical value for the achievement of plane strain conditions. Side-grooved specimens displayed the plane strain value of K_{IH} to a somewhat smaller critical width.

In view of the above findings, further tests were conducted on the effects of some alcohols and alkanes on the SCC susceptibility of a Ti-8Al-1Mo-1V alloy with the following measured characteristics:

Table C-2
Characteristics of Ti-8Al-1Mo-1V Alloy
(WT orientation, 123-ksi yield strength, 48 ppm hydrogen)

	K_{IX} (ksi $\sqrt{\text{in.}}$)	K_{IH} (ksi $\sqrt{\text{in.}}$)	K_{ISCC} (3.5% NaCl-water) (ksi $\sqrt{\text{in.}}$)
Thin Specimen (1/4 in.)	75	60	24
Thick Specimen (1/2 in.)	83	40	24

It was found that in the alkanes from methane through n-decane, K_{ISCC} values of about 40 ksi $\sqrt{\text{in.}}$ were produced in both the thin and thick specimens. Thus, as in salt water, there appeared to be little effect of specimen width. Because

the K_{IH} value of the thick specimens was also about $40 \text{ ksi} \sqrt{\text{in.}}$, no degradation in K_{ISCC} was observed in the alkanes. However, the alkanes apparently did produce cracking in thin specimens that otherwise would not have propagated cracks, since the thin specimens had a K_{IH} value of $60 \text{ ksi} \sqrt{\text{in.}}$

The same behavior was observed in the alcohols with three or more C atoms. In methanol and ethylene glycol, K_{ISCC} values of about $24 \text{ ksi} \sqrt{\text{in.}}$ were obtained, regardless of specimen width. Thus, these environments are more severe than the alkanes and produce threshold values identical to those produced by salt water. Methanol and ethylene glycol, unique among the organic environments, were also found to initiate cracks in smooth specimens loaded near the yield strength.

It was suggested previously (see ARPA Second Quarterly Report, Abstract 3, p. 34) that some of the alcohols may react with a fresh titanium surface to form an alkoxide and hydrogen, producing cracking through a mechanism involving hydrogen. No reason to discard this idea has been generated by the new data. The petroleum type of cracking reaction, proposed previously (see ARPA Second Quarterly Report, Abstract 3, p. 34) to explain the effects of some of the alkanes, appears now to be rather suspect. This is because it has been observed that methane also produces crack propagation.

One interesting test of the hydrogen mechanism hypothesis has been proposed. If hydrogen is indeed a harmful agent, an oxidizing salt added to salt water or to methanol might serve to absorb the electrons generated in a corrosion reaction, prevent the reduction of hydrogen ions to atomic hydrogen, and thereby raise K_{ISCC} . Additions of CuCl_2 , $\text{K}_2\text{Cr}_2\text{O}_7$, and HgCl_2 to water, salt water, and methanol did indeed raise K_{ISCC} , in some cases to the level of K_{IH} (from $24 \text{ ksi} \sqrt{\text{in.}}$ to $40 \text{ ksi} \sqrt{\text{in.}}$). The test is also of interest in connection with hypotheses that require the presence of chloride ions.

Preliminary tests on Ti-6Al-4V alloys and on steels in organics have been conducted with due attention to the values of K_{IH} . The tests on two Ti-6Al-4V alloys show that both are susceptible to cracking in methanol, but neither in salt water. The apparent susceptibility of one of the alloys in salt water was obviously a reflection of the difference between K_{IX} and K_{IH} .

The tests on high-strength steels have indicated generally very high values of K_{IH} relative to K_{IX} and much greater resistance to SCC in methanol than in salt water. The steels tested so far are AISI 4340 steel (220-ksi YS), 18 Ni maraging steel (200-ksi YS), and 12Ni-5Cr-3Mo maraging steel (180-ksi YS).

D. FRACTURE MECHANICS

Lehigh University

Studies of stress conditions as they affect stress-corrosion cracking are continuing. The main stream of the effort is directed at two phenomena in stress-corrosion cracking, i.e.,

1. Models of crack growth mechanisms
2. Models for arrest (or non-propagation) of cracks (K_{ISCC})

Theoretical studies at the elastic continuum model level have for all practical purposes been completed. The field equations for blunted elastic cracks were derived* (which reduce to the crack tip field equations for zero radius crack tips). From these equations, it was for example established that to propagate a stress-corrosion crack via a dissolution (degradation of ability to carry stress) mechanism the dissolution rate must depend upon stress to the 1/2 or higher power. This result appears to be true regardless of plasticity or other stress relaxation mechanisms and may be a key factor in crack arrest mechanisms, i.e., phenomenon 2; since crack arrest at K_{ISCC} may be a most important practical point for consideration in high-strength metal alloys, extensive experimental studies of the crack blunting mechanism have been initiated. First, available data on observations of blunting are being collected. Studies of blunting in metal alloys are continuing at Lehigh; to date, some sections of cracks in aluminum

* Creager, Matthew, "The Elastic Stress Field Near the Tip of a Blunt Crack", M.S. Thesis, Lehigh University, 1966.

See Also:

Creager, Matthew and P. Paris, "Elastic Field Equations for Blunt Cracks with Reference to Stress Corrosion Cracking", submitted to the International Journal of Fracture Mechanics.

alloys have shown blunting is affected by location along a crack front. The work to follow has three phases:

1. Collection of additional data on blunting in the "usual" precracked stress-corrosion cracking tests.
2. Critical experiments for examining blunting in metal alloys in water, temperature effects, electrochemical effects, etc., and critical experiments for examining blunting using special materials and environments (such as glass-water, mica-water, etc.).
3. Further refinements of analysis of the mechanical stress conditions (such as plasticity effects and non-continuum stress details).

It is hoped that these studies will not only lead to a better understanding of K_{Isc} but that it will also lead to better understanding of mechanical stress effects in crack growth mechanisms.

In addition to the stress analysis and modeling studies, a special study on thoroughly characterizing the glass-water stress-corrosion cracking phenomenon is being initiated.

Carnegie-Mellon University

To gain some more insight into the problem of moisture-enhanced crack growth in high-strength metal alloys, a series of experiments have been started to examine the effects of distilled water, hydrogen, and oxygen on the rate of fatigue crack propagation over a range of test temperatures. Dehumidified high-purity argon (99.9995 percent purity) is used as a reference dry environment. The materials to be examined will be a high strength aluminum alloy and a medium-carbon low-alloy ultrahigh strength steel.

Experimental work is well underway on a 1/4-in.-thick plate of commercial 7075-T651 (bare) aluminum alloy. Center-notched specimens are used. Fatigue crack growth experiments are carried out in an Amsler High Frequency Vibrophone operated at 143 cycles per second. A continuous recording electrical-potential system is used for monitoring crack growth. This system (patterned after one developed by Li and Wei, 1966, Materials Research and Standards, ASTM, Vol. 6, No. 8, p. 392) provides an average measurement sensitivity of 0.006 in. in half-crack length per 0.1 μ v change in potential for the 1/4-in. aluminum specimens, using a working current of about 5 amperes. The overall system accuracy is estimated at about 1 percent.

Data obtained thus far indicated that (1) fatigue crack propagation in this alloy is controlled by thermally activated processes with an apparent activation energy of several thousand calories per mole in the temperature range, 300-400°K, (2) water has a pronounced effect on the rate of fatigue crack propagation, increasing the growth rate by more than one order of magnitude over that observed in the reference dry argon environment at room temperature, and (3) there is little enhancement of crack growth by the dry hydrogen and dry oxygen environments, suggesting the importance of the water-metal reaction. Definite conclusions will have to await completion of the present series of experiments and companion metallographic study.

Georgia Institute of Technology

Several techniques are currently in use for the study of crack growth in stress-corrosion specimens. These include the optical, dial-gauge, electrical resistance, and compliance methods. Only the last two allow continuous monitoring of the crack growth. These methods, however, suffer from the disadvantage of undue complexity and limitations.

In the present work an attempt is being made to develop a simpler technique that will permit continuous monitoring of crack growth. Thus far, three approaches have been

taken. (1) A cantilever-beam stress-corrosion apparatus has been instrumented with a differential transformer to measure beam deflection; (2) a microphone is used to record acoustic emission; and (3) a single-transducer ultrasonic pulse-echo apparatus provides a continuous monitoring of the growth of the crack. Preliminary results have been obtained using 4150 tool steel specimens heat treated to 1525°F and quenched in oil; the stress intensity parameter was $K_I = 7 \text{ ksi} \sqrt{\text{In.}}$. The corrosive medium was 3.5 percent salt water solution. A constant-load stress-corrosion apparatus fashioned after the design developed at NRL has been used for the tests.

The ultrasonic technique involves clamping a piezoelectric transducer to the end of the specimen which is opposite the lever arm of the apparatus. The transducer sends out longitudinal waves in the direction perpendicular to the plane of the crack. The echo pulse due to the presence of the notch and crack is then electronically monitored (see Figure D-1). The specimen dimensions were 8 in. long, 0.5 in. wide, and 1 in. high, and the transducer was situated 5 in. from the notch. As the crack propagated, the height of the pulse was seen to increase. Figure D-2 displays a recorder trace of the output from the electronic gate which monitored the area under the "notch" pulse as a function of time. The voltage is proportional to the length of the crack as it propagates through the specimen. In the test that corresponds to Figure D-2, the crack propagated a distance of 12 mm before the overstress condition was reached and brittle fracture of the specimen occurred. In the above test, the plane stress condition was satisfied and the crack interface was fairly smooth and perpendicular to the long dimension of the specimen. At the top of Figure D-2 is seen a record of the beam deflection. The major features of the two displays are in agreement, that is, an increase in the rate of deflection corresponds to an enhanced crack growth velocity.

It has been observed in the course of this work that details in the oscilloscope pattern of the "notch" echo pulse are related to the mechanics of crack growth. For example, a sudden change in the plane of the propagating crack was correlated with an increase in the height of subsidiary peaks within the "notch" pulse. Therefore, it

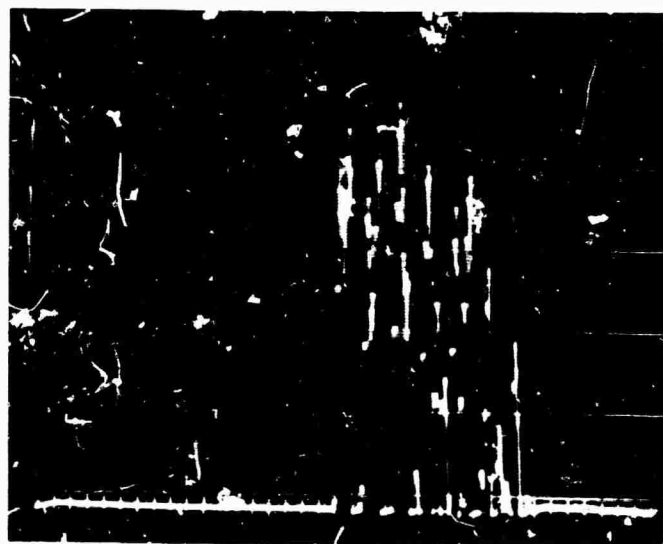
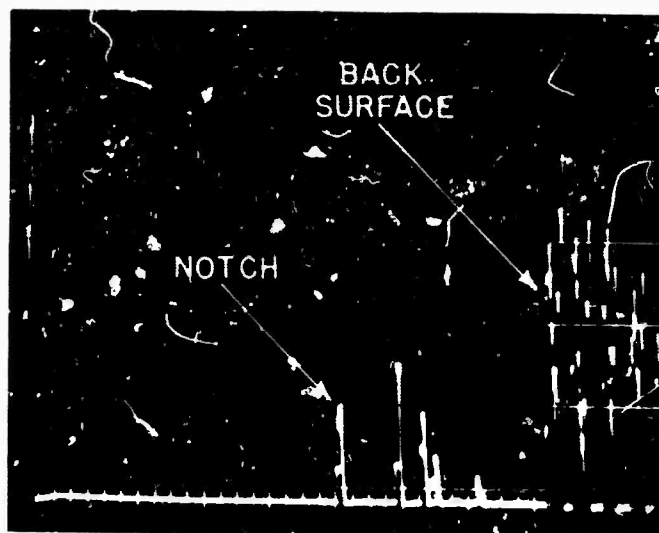


Figure D-1 - Reflected pulses of longitudinal ultrasonic wave used to monitor stress-corrosion crack propagation.

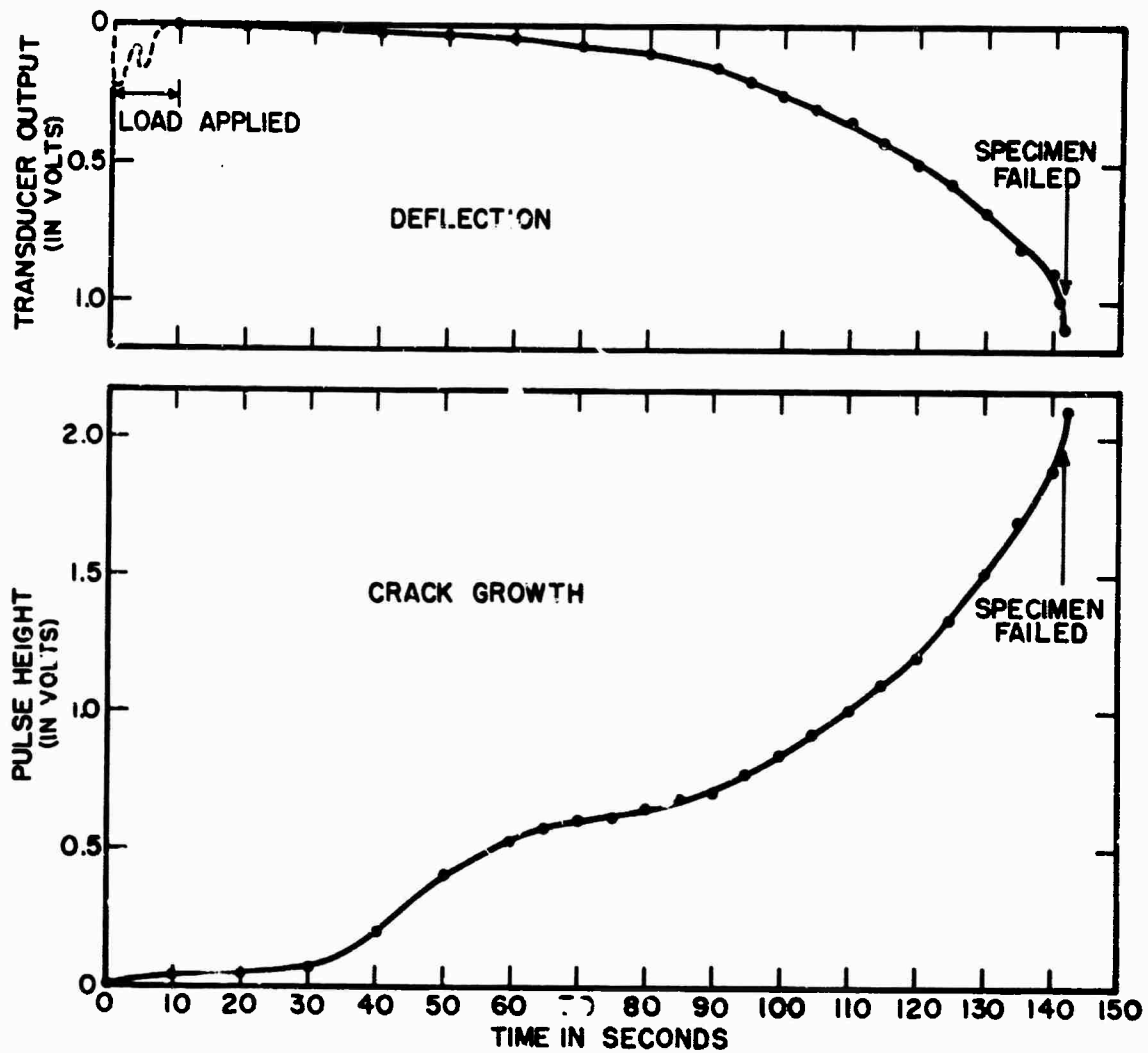


Figure D-2 - Crack growth as monitored by deflection (above) and reflected ultrasonic pulse height (below).

was decided to apply the contourograph technique, thus far only used in biomedical studies, to obtain a permanent record of crack growth mechanics.

The contourograph technique consists of supplementing the two-dimensional oscilloscope display of a train of pulses involving intensity modulation and a time base by a linear vertical sweep of the pattern. Using this technique, changes in the electrocardiogram patterns over a period of minutes or hours have been displayed with great advantage. When applied to metallurgy this technique should allow detailed study of the mechanics of a growing crack. It may also be possible to observe blunting of cracks during test under various experimental conditions.

The ultrasonic technique is limited to detecting cracks that present a reflecting area with dimensions greater than $\lambda/2$, where λ is the wavelength of ultrasonic waves in the material involved. It appears that it should be possible to detect increases in crack length of the order of 0.2 mil in steel using a 5 Mc transducer. The crack growth studies in stress corrosion using ultrasound will be supplemented in the future by data from acoustic emission at ultrasonic frequencies.

National Research Laboratory

Utilizing a recent analysis by Krafft (1) estimates of local dissolution velocity (v_p) were calculated for Ti-8Al-1Mo-1V alloy (NRL T-19) from the plastic flow properties and stress-corrosion data in different organic media obtained by Sandoz (2). By this method, although the shelf level of K_{Iscc} is constant, the values of v_p diminish in inverse proportion to the carbon chain length of the alcohols (3). This is not so obvious in the case of the hydrocarbons, but less actual fracture data were available.

v_p as here determined is felt to provide a somewhat more sensitive discrimination criterion than do the values of K_{Iscc} .

Utilizing compliance techniques for continuous crack length measurements (beam strain detectors inserted in the notch

for deflection measurement) and time signals fed into the X-Y Recorder (Moseley) to amplify the load-deflection curve at appropriate intervals. Attempts have been made to determine K_I vs crack velocity (V_C) for several specimen configurations. The specimens were subjected to a constant load while immersed in a 3.5 percent NaCl solution contained in a polyethylene vessel.

The parallel-sided double cantilever beam (DCB) has not proven satisfactory; regardless of crack orientation with respect to rolling direction the arms of the beam tended to break off before sufficient crack run for useful results. Furthermore, as has been previously noted in this laboratory, the crack path tends to lie outside the side notch root, thus rendering calculations compensatory for B/B_n ratio somewhat questionable.

Use of the single-edge-notched (SEN) specimen obviated some of these side effects. However, with the relatively thin specimens dictated by the testing machine capacity, it was noted that the crack continued to grow long after a value indicative of K_{Ic} was determined. This certainly indicates that plane strain conditions no longer operated, but the specimen size was definitely insufficient for K_{Ic} (plane stress) determination.

Such measurements as were obtained from SEN specimens of Ti-7Al-2Mo-1V alloy (NRL T-89) indicated increases in crack velocity (V_C) with K_I and a tendency for acceleration in the neighborhood of K_{Ic} (asymptotic velocity).

Since it seemed advisable to isolate situations of plane strain for first measurements, beams of sufficiently large size to contain the expected plastic zone have been prepared both of the aforementioned Ti-7Al-2Mo-1V (T-89) and Ti-8Al-1Mo-1V (T-19) alloys. These will be tested in three-point bending, utilizing the same instrumentation and experimental conditions. Hopefully, data can be reported in the next quarterly report.

Difficulties of preventing capillarity induced the presence of some galvanic action between the titanium specimen and the steel deflection beams; these are, therefore, now being made of a compatible alloy.

The validity of the "Ligamental Erosion Model" for stress-corrosion cracking proposed by Dr. J. M. Krafft was examined by application of the model to fifteen different titanium alloys whose stress-corrosion cracking characteristics were known. The fifteen alloys were selected to represent a wide range of all mechanical properties, including salt water stress-corrosion cracking resistance.

The study showed that while the model can be correlated with stress-corrosion cracking data points determined by fractured specimens, it cannot successfully predict the stress-corrosion cracking threshold (K_{ISCC}). The threshold is determined by "no-break" points in the cantilever bend test. These points are also those not in agreement with the model. A closer examination of the results showed that the stress-corrosion cracking threshold levels predicted by the model were remarkably similar, while the measured levels varied widely. An investigation of effects of fatiguing methods on one alloy indicated that this was not a factor in the discrepancy between the actual and predicted stress-corrosion cracking levels.

References

1. J. M. Krafft, "Role of Dissolution in Corrosion-Assisted Cracking of Titanium Alloys," Report of NRL Progress, March 1967. p. 6
2. G. Sandoz and R. Newbegin, "High Strength Alloy Under Stress in Corrosive Environments (Some Environmental Effects on Titanium Alloys)," Report of NRL Progress, March 1967. p. 28
3. A. M. Sullivan, "High Strength Alloys Under Stress in Corrosive Environments (Dissolution Velocities of Different Organic Media)," Report of NRL Progress, April 1967. p. 18

E. ABSTRACTS OF MANUSCRIPTS AND REPORTS

1. H. R. Smith, D. E. Piper and F. K. Downey, "A Study of Stress-Corrosion Cracking by Wedge-Force Loading," Document D6-19768, June 1967, The Boeing Company

Abstract

Wedge-force loading a center-cracked sheet specimen provides a unique resolution of whether stress-corrosion cracking (SCC) depends on an applied crack-tip stress-intensity factor or on net-section stresses. With this loading, crack extension causes a decreasing stress-intensity factor at the crack tip, while the net-section stresses increase. Therefore, when stress-corrosion crack growth is arrested in this specimen, the dependency on stress intensity is proved. The stress intensity at arrest agrees remarkably well with K_{SCC} values determined by more conventional techniques that establish crack initiation thresholds through multiple tests. Crack growth rate data important to the establishment of inspection intervals in structure can also be obtained. Finally, the technique affords considerable economy of test time and material costs in stress-corrosion studies.

2. N. M. Lowry, O. R. Mulkey, J. M. Kuronen, and J. W. Bieber, "A Method of Measuring Crack Propagation Rates in Brittle Materials," Document D6-60072, May 1967, The Boeing Company

Abstract

A method of measuring the rate of crack propagation is described. The method, applicable to any specimen having a smooth surface across which brittle-type fracture will occur, is accomplished by means of a fine gridwork of conducting lines applied to the specimen by various vacuum deposition techniques. When a potential is applied to the grid, a direct reading of current (or distance) versus time is obtained with a strip chart recorder or equivalent device. The method has been applied to the study of brittle-type fracture associated with stress corrosion cracking observed in titanium alloys.

3. B. F. Brown, "The Fracture Mechanics of Stress-Corrosion Cracking," Submitted to Metallurgical Reviews

Abstract

A review of experimental methods, plastic zone effects, kinetics, and translation of laboratory data to design.

4. G. M. Sinclair and S. P. Withrow, "Environmentally Assisted Crack Growth in Glass," NRL Memorandum Report (in press)

Abstract

Glass exhibits the properties of high compressive strength and low density which make it of interest for deep ocean applications. However, the surface of unprotected glass contains flaws which grow under low stress in moist conditions to critical size for failure.

Various methods were used to investigate and increase the reliability of glass under stress. Data was obtained on failure of unprotected glass plates subjected to biaxial tension in 50% R.H. Analysis by extreme value statistics indicated the failure condition could be represented by a plane surface in extreme value probability, log stress, log time space. Removal of surface flaws by etching in 5% aqueous HF increased the mean failure strength from approximately 30 ksi with a value of 300 ksi biaxial tension being attained in one case.

Increases in lifetimes of one, two and three orders of magnitude were obtained by protecting the glass from atmospheric moisture by preheating and coating with petrolatum, preheating glass and coating with preheated petrolatum, and experimenting at -30°F, respectively. Some improvement in minimum time to failure was obtained by eliminating the weaker specimens by proof testing.

5. R. W. Judy, Jr. and R. J. Goode, "Stress-Corrosion Cracking of Alloys of Titanium in Salt Water," NRL Report 6564 (in press)

Abstract

The salt water stress-corrosion cracking (SCC) characteristics have been determined for a large number of titanium alloys representative of commercial production. These data were compiled as part of an NRL program directed to determining the underlying principles of SCC in metals and to establishing procedures for improving the SCC resistance of these metals as well as learning to tolerate the problem where it exists.

The SCC resistance was determined using a pre-cracked cantilever bend specimen with analysis by fracture mechanics techniques. Test results presented for the spectrum of alloys and weldments studied indicate that no correlation with mechanical properties exists, which makes precise prediction of SCC properties of particular alloys difficult, if not impossible.

The data in this report are presented to provide guideline information for programs similar in nature to the NRL program as well as for alloy development, design and materials selection, and specifications and quality control.

6. A. M. Sullivan, "Dissolution Velocities of Different Organic Media," Report of NRL Progress, April 1967, pp. 18-19
7. E. P. Dahlberg, "Thin Foil Electron Microscopy," Report of NRL Progress, April 1967, pp. 19-21
8. G. Sandoz, "Delayed Fracture Characteristics of Ti-8Al-1Mo-1V Alloy," Report of NRL Progress, May 1967, pp. 31-32

F. TITLES OF PREVIOUS REPORTS AND PAPERS

1. Matthew Creager, "The Elastic Stress Field Near the Tip of a Blunt Crack," (Master's Thesis) Lehigh University October 1966
2. E. P. Dahlberg, "An Annotated Bibliography of Recent Papers and Reports on the Subject of Ambient Temperature Aqueous Stress-Corrosion Cracking of Titanium and Titanium Alloys," NRL Bibliography Report 29, October 1966
3. E. P. Dahlberg (General Editor), "ARPA Coupling Program on Corrosion (First Quarterly Report)," NRL Memorandum Report 1739, December 1966
4. R. W. Judy, Jr. and R. J. Goode, "Stress-Corrosion Cracking Characteristics of Alloys of Titanium in Salt Water." NRL Report 6564. February 1967
5. G. Sandoz and R. L. Newbegin, "Stress-Corrosion Cracking Resistance of an 18Ni 200 Grade Maraging Steel Base Plate and Weld," NRL Memorandum Report 1772, March 1967
6. G. Sandoz, "Effects of Some Organics on the Stress-Corrosion Susceptibility of Some Titanium Alloys," Conference Summary Report (Accelerated Crack Propagation of Titanium by Methanol, Halogenated Hydrocarbons, and other Solutions, March 1967), to be published by DMIC, Battelle Memorial Institute
7. George Sandoz and R. L. Newbegin, "Stress and Corrosive Environments (Some Environmental Effects on Titanium Alloys)," Report of NRL Progress, March 1967, pp. 28-30
8. G. Sandoz, "Stress-Corrosion Cracking Susceptibility of a Titanium Alloy in a Non-electrolyte," Nature, Vol. 214, April 8, 1967, pp 166-167

9. E. P. Dahlberg (General Editor), "ARPA Coupling Program on Stress-Corrosion Cracking (Second Quarterly Report)," NRL Memorandum Report 1775, April 1967
10. C. O. Timmons, R. L. Patterson, and L. B. Lockhart, Jr., "The Adsorption of C-41 Labeled Stearic Acid on Iron," NRL Report 6553, June 2, 1967
11. D. A. Meyn, "Effect of Crack Tip Stress Intensity on the Mechanism of Stress-Corrosion Cracking of Titanium-6Al-4V in Methanol," to be published in Corrosion Science

G. ABSTRACTS OF SOME RECENT ARTICLES ON
STRESS-CORROSION CRACKING

1. R. P. Frankenthal, "The Inhibition of Pitting and Stress-Corrosion Cracking of Mg-Al Alloys by NO_3^- ," Corrosion Science, Vol. 7, No. 1, January 1967, p. 61

Abstract

It is shown that the nitrate ion will inhibit both pitting and stress-corrosion cracking of a Mg-6% Al alloy in potassium chromate-sodium chloride solution. Potential measurements indicate that the inhibition results from protection of the passivating film against breakdown.

2. J. C. Scully, "Kinetic Fractures of Stress-Corrosion Cracking," Corrosion Science, Vol. 7, No. 4, April 1967, p. 197

Abstract

Transgranular stress-corrosion cracking is discussed and explained by a mechanism the essence of which is the inadequate repassivation of emergent slip steps. It is argued that the importance of many of the phenomenological factors that have been used to explain stress-corrosion cracking lies in the influence that these factors exert on the repassivation kinetics. The interdependence of metallurgical substructure and electrode kinetics is a particular feature of the proposed mechanism which is discussed with particular reference to austenitic stainless steel and titanium alloys. Its wider application to intergranular cracking is briefly described.

3. Sara J. Ketcham, "Polarization and Stress-Corrosion Studies of an Al-Cu-Mg Alloy," Corrosion Science, Vol. 7, No. 6, June 1967, p. 305

Abstract

The effect of slow quenching following solution heat treatment on naturally aged Al-Cu-Mg alloy can be detected by corrosion potentials and accelerated corrosion tests for intergranular corrosion and stress-corrosion susceptibility. Faster quenching rates give no indication of the existence of any continuous anodic paths until a stress is applied. A possible mechanism for this is proposed based on the electrochemical effect of stress.

4. J. A. S. Green and E. G. Haney, "Relationships Between Electrochemical Measurements and Stress-Corrosion Cracking of Maraging Steel," Corrosion, Vol. 23, No. 1 January 1967, p. 5

Abstract

Stress-corrosion cracking of 18 Ni maraging steel foil has been studied in deionized water solutions with the pH adjusted by Na OH additions over a range from 8 to 13. The full range of NaCl contents from saturated solutions to no addition was tested with specimens stressed to 75 percent of yield strength. For each variation in NaCl content, the specimen failure times go through a minimum with respect to pH. With increasing NaCl content, the minimum becomes more pronounced and its position shifts towards higher pH values. The position of each minimum is indicated by electrode potential measurements. Potentiostatic measurements as a function of pH confirm that maximum susceptibility to stress-corrosion cracking occurs just prior to the onset of passivation.

5. R. A. Miller, J. R. Myers, and R. K. Saxer, "Stress Corrosion of Beryllium in Synthetic Sea Water," Corrosion, Vol. 23, No. 1, January 1967, p. 11

Abstract

Continuous total immersion testing of pickled beryllium sheet material in synthetic sea water revealed that corrosion rate decreases asymptotically from about 21.5 to 2.0 mpy as exposure period increased from 5 to 150 days. Beryllium was observed to be susceptible to severe pitting attack. Testing established that beryllium is susceptible to stress-corrosion when exposed to synthetic sea water. Time-to-failure decreased from about 2340 to 40 hours as applied tensile stress was increased from 1220 to 40,000 psi. Electron fractography studies suggested that stress-corrosion failure occurred transgranularly.

6. T. R. Beck, "Stress-Corrosion Cracking of Titanium Alloys," J. of the Electrochemical Society, Vol. 114, No. 6, June 1967, p. 551

Abstract

Stress-corrosion cracking of Titanium 8%Al-1%Mo-1%V alloy notched tensile specimens was investigated in various salt solutions under potentiostatic conditions. Stress-corrosion cracking of duplex annealed Ti-8-1-1 alloy occurred in chloride, bromide, and iodide solutions but did not occur in other solutions such as fluoride hydroxide, sulfide, sulfate, nitrate, or perchlorate. The ultimate strength was strongly dependent on potential. The velocity of crack propagation and current flowing into the crack in chloride bromide, and iodide solutions were linearly related to the applied potential above a potential of ~900 mv to the saturated calomel electrode. An electrochemical mechanism controlling the velocity is implied.

7. T. J. Smith and R. W. Staehle, "Role of Slip Step Emergence in the Early Stages of Stress-Corrosion Cracking in Face-Centered Iron-Nickel-Chromium Alloys," Corrosion, Vol. 23, No. 5, May 1967, p. 117

Abstract

Thin foils of four face centered cubic iron-nickel-chromium alloys and of pure iron and pure nickel have been examined in the electron microscope before and after exposure to boiling $MgCl_2$. Evidence of parallel dissolution arrays in stressed thin foils was taken as confirmation of formation of slip steps by dislocations which move while specimens are in intimate contact with an active environment. The faulted region exposes non-protected base metal with the result that rapid local dissolution occurs along an axis of the active slip plane. Because parallel dissolution arrays occur in susceptible as well as non-susceptible alloys, the process of slip step activated dissolution is taken to be necessary, but not critical in stress-corrosion cracking. Evidence is presented to suggest that neither dislocation coplanarity (as shown in thin foils) nor dislocation reactivity are factors in stress-corrosion cracking in austenitic Fe-Ni-Cr alloys. The emergent slip step model is hypothesized to be useful in interpreting propagation phenomena and grain size effects in stress-corrosion cracking susceptibility.

8. M. H. Peterson, B. F. Brown, R. L. Newbegin, and R. E. Groover, "Stress-Corrosion Cracking of High Strength Steels and Titanium Alloys in Chloride Solutions at Ambient Temperature," Corrosion, Vol. 23, No. 5, May 1967, p. 142

Abstract

By using a precracked cantilever-loaded test specimen, a relatively rapid and economical method of studying stress-corrosion cracking in chloride solutions was developed. The method permits testing sensitivity of specimens to stress-corrosion cracking in a fraction of the time required for smooth specimens.

Both high strength steels and titanium alloys proved susceptible in flowing sea water. AISI 4340 heat treated to strengths up to 225 ksi showed stress intensity increasing as the crack grew. Stress cracking of Ti-8Al-1V occurred at a final velocity of 1/4 in. per minute.

Cathodic protection of high strength steel was not found to be a reliable means of preventing stress-corrosion cracking because of close potential control required. At potentials created by a steel-zinc couple, it cracked at a stress intensity much lower than was the case for a freely corroding specimen.

9. E. Snape, "Sulfide Stress-Corrosion of Some Medium and Low Alloy Steels," Corrosion, Vol. 23, No. 6, June 1967, p. 154

Abstract

A study made of factors influencing sulfide-stress corrosion of a number of low alloy and medium alloy steels showed that their delayed failures when exposed simultaneously to stress and the corrosive action of acidified brine-hydrogen sulfide solutions have most of the features of hydrogen induced, delayed brittle failures. Different steels subjected to the same exposure conditions showed varying degrees of embrittlement as measured by ductility loss in bend tests.

Ductility could be restored partially by room temperature storage. Ductility restoration was related to the amount of hydrogen removed after exposure.

Delayed failure under stress occurs when corrosion generated hydrogen is absorbed, and lowers fracture strain until it equals the strain under load.

A minimum applied stress was obtained for each steel below which failure did not occur. This "threshold" stress decreased as strength level increased and depended simultaneously on composition and microstructure.

Nickel had little effect on cracking behavior of a steel whereas carbon appeared to be detrimental. Twinned martensite was more susceptible than untwinned martensite. Steels containing austenite were more resistant than body-centered steels.

10. H. A. Holl, "Deformation Substructure and Susceptibility to Intergranular Stress-Corrosion Cracking in an Aluminum Alloy," Corrosion, Vol. 23, No. 6, June 1967, p. 173

Abstract

Dislocation arrangements in a deformed aluminum zinc-magnesium-copper alloy aged to various states of susceptibility to stress-corrosion cracking have been examined by transmission electron microscopy. Material in a highly susceptible condition deforms in a characteristic manner; slip is concentrated in well defined bands and dislocations show a marked tendency to remain on their original slip planes. In material exhibiting a low susceptibility, restricted slip does not occur and dislocations form uniformly distributed tangles. These results are interpreted in terms of existing models for intergranular stress-corrosion cracking. It is concluded that when this alloy is aged to contain G.P. zones or coherent precipitates it will be highly susceptible to stress-corrosion cracking, whereas when aged to contain non-coherent precipitates the alloy will be highly resistant.

11. G. J. Petrak, "Dynamic Subcritical Crack Growth Properties of Duplex Annealed Ti-8Al-1Mo-1V and Mill Annealed Ti-6Al-4V in an Air and Corrosive Environment," Technical Report AFML-TR-66-392, January 1967, University of Dayton Research Institute

Abstract

This program was conducted to determine the dynamic (fatigue) crack growth properties of two titanium alloys (Ti-8Al-1Mo-1V Duplex Annealed and Ti-6Al-4V Mill Annealed) at room temperature in an air and in a 3.5 percent NaCl environment. Dynamic crack growth versus cycles to failure was determined at two loading frequencies (40 cpm and 2 cpm) for the corrosive environment and at a 40 cpm loading frequency for the air environment. A comparison of the air and corrosive environment test data at the 40 cpm loading frequency shows a reduction in cyclic life when exposed to the 3.5 percent NaCl environment. Also a comparison of the corrosive environment test data at loading frequencies of 40 cpm and 2 cpm shows a reduction in cyclic life on both a time and a number of cycles to failure basis at the higher loading frequency.

12. F. H. Haynie, D. A. Vaughan, D. I. Phalen, W. K. Boyd, and P. D. Frost, "A Fundamental Investigation of the Nature of Stress-Corrosion Cracking in Aluminum Alloys," Technical Report AFML-TR-66-267, January 1967, Battelle Memorial Institute

Abstract

A statistically designed experiment to study the effects of metallurgical variables on stress-corrosion cracking behavior of high-purity 7039- and 7079-type alloys has revealed several important facts. Stress-corrosion-cracking susceptibility is a function of the stress normal to the grain boundaries rather than a function of the applied stress on these materials in thin sheet and plate form.

The combined results of electrochemical, autoradiographic, electron-transmission, and electron-replica studies strengthen the belief that cathodically produced hydrogen dissolved in strained grain boundaries is essential for the initiation of stress corrosion cracking in these alloys. Based on these results a mechanism is proposed. This proposed mechanism involves the absorption of cathodically produced hydrogen into tensile-strained, mechanically weak (alloy-depleted zones) grain boundaries. The hydrogen acts to reduce the activation energy for anodic dissolution of the metal and thus accelerates the localized corrosion at the grain boundaries perpendicular to applied tensile stresses.

13. A. J. Jacobs, "Study of Stress-Corrosion Cracking of Aluminum Alloys," Final Report R-7026, Contract NOw 66-0309d, Naval Air Systems Command, North American Aviation, Inc.

Abstract

A further clarification of the mechanism of stress-corrosion cracking in 7075 aluminum alloy was obtained, particularly with regard to the role of dislocations in the mechanism and to the relationship between dislocation mobility and susceptibility to stress-corrosion cracking; high dislocation mobility reduces susceptibility. It was demonstrated during stress-corrosion tests on 7075-T73 specimens that had undergone prior plastic deformation, that the introduction of dislocations alone did not lower the dislocation mobility sufficiently to diminish the stress-corrosion resistance.

Fractographic analysis revealed that this was a true intergranular, stress-corrosion failure, similar in every respect to a stress-corrosion failure in 7075-T6 alloy. A slip-line study of progressively deformed 7075-T6 and -T73 alloys indicated that slip takes place throughout the grain and is not confined to the grain boundary margins, thus leading to the ultimate transgranular, ductile type of fracture that is observed in fractographs.

14. D. L. Piper, S. H. Smith, and R. V. Carter, "Corrosion Fatigue and Stress-Corrosion Cracking in Aqueous Environments," Document D6-60067, March 1967, The Boeing Company

Abstract

Corrosion fatigue and stress-corrosion cracking of titanium alloys in sodium chloride solution were found to depend on composition, thickness, and heat treatment. The test specimen configurations used to measure susceptibility to these phenomena yielded data amenable to analysis by fracture mechanics methods and thus afforded a positive system of fracture control in corrosive aqueous environments.

15. T. R. Beck, M. J. Blackburn, "Stress-Corrosion Cracking of Titanium Alloys: Electrochemical Mass-Transport-Kinetic Model, Metallurgical and Mechanical Effects, and Proposed Relation of Electrochemical, Metallurgical and Mechanical Effects," Quarterly Progress Report No. 4, Contract NAS 7-489, June 1967, The Boeing Company

Abstract

A continuum electrochemical mass-transport-kinetic model has been formulated and computations have been made on a digital computer, giving results that appear to be consistent with velocity-current-potential data for duplex annealed Ti:8-1-1. The model predicts that the electrochemically controlled velocity is determined by mass transport of chloride, bromide or iodide ions to the crack tip. The tip current is equivalent to formation of an adsorbed monolayer of halide ions or titanium halide. Data on the relation of velocity to bulk halide ion concentration indicates that a recycling of halide ions by displacement or hydrolysis occurs near the tip. Many similarities are observed to the previously proposed model for pitting corrosion of titanium.

Ti:8-1-1 heat treated to a very brittle condition and Ti-Al alloys after similar heat treatment give stress-corrosion cracking velocities greater than predicted from the electrochemical model, indicating an additional mechanical mode of fracture. This mechanical mode is related to rate of change of stress intensity. The velocity in the electrochemical mode appears to be related linearly to stress intensity factor, perhaps through changes in crack angle. Ti:8-1-1 heat treated to a ductile condition gives stress-corrosion cracking velocities less than predicted from the electrochemical model. It is proposed that ductile (non-susceptible) phases retard crack propagation in this case.

16. T. R. Croucher, "Stress Corrosion Testing," Materials Protection, Vol. 6, No. 8, August 1967, p. 44

Abstract

The author reports on a joint test program conducted by 15 companies on four precipitation hardening semiaustenitic steels to determine a standard stress corrosion test procedure. Two specimen configurations (C-ring and bent beam) and two environments (20% salt spray and 3-1/2% salt alternate immersion) were evaluated. The results showed that the bent beam specimens provided consistent, repeatable, and stress dependent data, while data obtained using the C-ring specimens were scattered and nonreproducible. The 20% salt spray was sufficiently severe to fail specimens in the 1,000-hour test cycle, while the alternate immersion test in 3-1/2% sodium chloride proved ineffective in causing reproducible failures.

17. H. P. Leckie, "Stress-Corrosion Characteristics of a Ti-7Al-2Cb-1Ta Alloy," Corrosion, Vol. 23, No. 7, July 1967, p. 187

Abstract

With only a few exceptions, titanium and its alloys have been considered immune to stress-corrosion cracking in almost all environments at room temperature. It has been shown recently, however, that titanium alloys will fail readily by stress-corrosion cracking when a notched specimen is exposed using the cantilever-beam loading technique.

This study reports the stress-corrosion behavior of a Ti-7Al-2Cb-1Ta alloy evaluated using the cantilever-beam testing procedure. The evaluation included effects of applied anodic and cathodic potentials, specimen loading method and presence of hydroxyl ion as inhibitor.

When a specimen was loaded in air, stress-corrosion cracking could be almost eliminated by allowing the protective oxide film, ruptured by stress, to heal before adding the electrolyte. Stressing the specimen and thus rupturing the passive film in a chloride environment, however, resulted in a very pronounced susceptibility to stress-corrosion cracking and short times to failure.

Potentials more active than -1.3 volts (versus saturated calomel electrode) afforded cathodic protection to the alloy tested, which, surprisingly, appeared to be immune to hydrogen embrittlement.

The present studies have shown that the stress-corrosion cracking of this titanium alloy is caused by the rupturing of the protective oxide film followed by stress-corrosion cracking by an active path mechanism.

The following three reports are referenced by courtesy of the Commander, Naval Ship Engineering Center, Code 6101D, Department of the Navy, Washington, D. C.:

18. A. W. Loginow, "Corrosion and Stress Corrosion of HY-130(T) Steel and HY-80 Steel in Marine Environments," Technical Report, Project No. 39.001-100(2), July 1967, U.S. Steel Applied Research Laboratory

Abstract

Studies were made to determine the corrosion and stress-corrosion properties of plain-plate and welded specimens of 5Ni-Cr-Mo-V steel—now designated HY-130 (T)—along with HY-80 steel for comparison purposes, in various marine environments. Included were shallow-water exposure tests conducted at Wrightsville Beach, North Carolina, and deep-sea exposure tests conducted in cooperation with the U. S. Naval Civil Engineering Laboratory at Port Hueneme, California.

In two-year tests, the corrosion behavior of HY-130(T) steel plain-plate specimens was essentially equivalent to that of HY-80 steel. The HY-130(T) steel weldments, however, showed appreciably less corrosion than HY-80 steel weldments in these tests. In addition, the difference in corrosion rates between the various areas of the HY-130(T) steel weldment was appreciably less than for the HY-80 steel and is considered insignificant. In the marine atmosphere the corrosion rates after two years of exposure were relatively low and about the same for both steels. Both steels—plain-plate and welded HY-80 and HY-130 (T)—were resistant to stress-corrosion cracking in the marine atmosphere and in sea water near the water surface. In the deep-sea tests, a delayed failure occurred in the weld metal of one of the HY-130(T) welded U-bend specimens.

19. A. W. Loginow, "Stress Corrosion of Maraging-Steel Weldments in Sea Water," Technical Report NObs-94535 (FBM) SF020-01-01, Task 854 B-63502-1, 1 August 1967, U.S. Steel Applied Research Laboratory

Abstract

Since 1963, the Applied Research Laboratory has been engaged in the development of steels with yield strengths in the range 180 to 210 ksi for use in submarine hulls. Although coating systems normally are applied to protect submarines from the corrosive action of sea water, these coatings deteriorate with time or they may become damaged, thereby exposing some areas of the steel to sea water. Hence, knowledge of the corrosion and stress-corrosion behavior of candidate steels in the uncoated condition is considered to be important in the characterization of steels for submarine-hull service. This report presents the results of stress-corrosion tests conducted on 12Ni-5Cr-3Mo and 18Ni-8Co-3Mo maraging steels in marine environments.

U-bend specimens of these steels were used in both welded and unwelded conditions and were prepared to simulate several welding and heat-treating sequences. The stressed specimens were exposed in quiescent and flowing sea water, in the tide zone, and in marine atmosphere. The results of these tests showed that welded and plain-plate 18Ni-8Co-3Mo and plain-plate 12Ni-5Cr-3Mo steel specimens did not crack in 750 days in any of the environments tested. Post-weld-aged 12Ni-5Cr-3Mo steel specimens cracked in about 140 days. Of the specimens that were not aged after welding, only the annealed and welded specimens exposed in the tide zone cracked (187 days); other specimens of this steel that were not post-weld-aged did not crack in 750 days. All observed cracks started in the weld and either progressed through the thickness of the specimens (consisting of weld metal and base metal) or stopped in the base metal.

20. S. R. Novak and S. T. Rolfe, "K_{ISCC} Tests of HY-180/210 Steels and Weld Metals," Technical Report NObs-94535 (FBM) SF020-01-01, Task 854 B-63105, B-63304, 1 August 1967, U.S. Steel Applied Research Laboratory

Abstract

As part of a continuing program to evaluate the susceptibility of candidate HY-180/210 weldments to stress-corrosion cracking, the susceptibility of five base metals and four weld metals was measured by testing fatigue-cracked cantilever-beam specimens of these materials in synthetic sea water. The results of these tests were expressed in terms of a plane-strain critical stress-corrosion-crack intensity factor, K_{ISCC}. The alloy systems evaluated in the present study included 12Ni-5Cr-3Mo maraging-steel weldments, Republic Steel Corporation 9Ni-4Co-0.25C weldments, 10Ni-Cr-Mo-Co dual-strengthened steel weldments, and rapidly heat-treated 5Ni-Cr-Mo-V steel plates.

The present results showed that (1) the resistance of the 12Ni-5Cr-3Mo maraging steel base metal and weld metal to stress-corrosion cracking was poor (K_{ISCC} values in the range 33 to 44 ksi $\sqrt{\text{inch}}$), (2) the resistance of the 9Ni-4Co-0.25C base metal was good (K_{ISCC} of 110 ksi $\sqrt{\text{inch}}$) but the resistance of the weld metal was moderately poor (K_{ISCC} of 60 ksi $\sqrt{\text{inch}}$), (3) the resistance of the 10Ni-Cr-Mo-Co base metals and weld metals was excellent (K_{ISCC} values in the range 130 to 155 ksi $\sqrt{\text{inch}}$), and (4) the resistance of the rapidly heat-treated 5Ni-Cr-Mo-V steel plate was good (K_{ISCC} of 118 ksi $\sqrt{\text{inch}}$).

In general, the present results show that, of all HY-180/210 weldment systems investigated to date, 10Ni-Cr-Mo-Co weldments exhibit the greatest resistance to stress-corrosion cracking. In addition, an analysis of the plane-strain conditions existing in the specimens employed in the present study indicated that the measured K_{ISCC} values are reliable enough to be used for general engineering purposes.

Additional studies are in progress to determine K_{ISCC} values for other promising HY-180/210 weldments and to assess the validity of K_{ISCC} as an invariant material property.

21. H. H. Johnson and P. C. Paris, "Sub-Critical Flaw Growth," Report No. 730, 25 July 1967, Material's Science Center, Cornell University

Abstract

The major evidence bearing upon sub-critical flaw growth in structural materials is reviewed and discussed. Attention is focused upon the growth of pre-existing flaws at operating stresses less than the net section yield strength, from both the separate and combined effects of fatigue and aggressive environments.

In Part 1 the applicability of fracture mechanics concepts to flaw growth is considered, and it is demonstrated that the stress intensity factor may be viewed as the driving force for both fatigue crack growth and environmental cracking under static load. This allows a correlation of test results from different specimen geometries, and also a correlation between test results and service failures.

Environmental cracking under static load is considered in Part 2. Steels and titanium alloys in various environments of water, water vapor, hydrogen, and oxygen are discussed. For steels crack growth in water and saturated water vapor is a thermally activated process. The crack growth activation energy agrees well with the measured value for diffusion of hydrogen. The role of oxygen in inhibiting sub-critical flaw growth in vapor environments is discussed.

Fatigue crack growth is considered in Part 3. It is shown that the stress intensity range is the major factor governing crack growth rates and fatigue life, with frequency and mean load as secondary variables. Crack growth rate laws are considered, and it is

demonstrated that the fourth power law holds over the widest range. For an astonishing variety of steels, the fatigue crack growth rate is insensitive to composition, microstructure, and strength level, when the growth rate is plotted as a function of the stress intensity range.

The combined effects of fatigue and aggressive environments are considered in Part 4. Some of the environmental behavior patterns in static loading are observed to carry over to fatigue loading. A lack of data for stress intensity ranges less than the threshold is noted.

In Part 5 engineering applications are emphasized. Relationships among flaw size, threshold stress intensities in different environments, and proof and operating stresses are presented graphically and their interpretation is discussed. For 4340 steel the role of yield strength level is summarized in a diagram which indicates that environmental cracking is the major problem at yield strengths in excess of 180 ksi, while fatigue crack growth is the major problem at lower strength levels.

22. K. R. Agricola and J. T. Snyder. "Stress Corrosion of Explosively Deformed High-Strength Alloys," ASM Metals Engineering Quarterly, Vol. 7, No. 3, August 1967, pp. 59-63

Abstract

Four high-strength steels and one high-strength aluminum alloy were evaluated before and after explosive deformation to establish the effects of forming on stress-corrosion resistance. Alternate immersion in a 3-1/2% NaCl solution for up to 200 hr. was accomplished. Specimens were stressed to 80% of the 0.2% offset tensile yield strength. Among the steels, only the 18% nickel maraging steel showed an appreciable effect of corrosion under stress on the reduction in mechanical properties. The 7039-T62 aluminum was also adversely affected. Explosive deformation

did not cause any detrimental effects on properties after alternate exposure for the steels evaluated; however, the effect of high-energy forming on corrosion susceptibility of 7039-T62 aluminum under stress was significant. Stress corrosion in the classical sense, that is, intergranular attack with subsequent crack propagation was not observed for any of the alloys.

H. DIARY OF EVENTS

The Annual Program Review Meeting of key Program personnel was held at the Carnegie-Mellon University, Pittsburgh, on 8-10 May, inclusive. In all, 101 persons attended this meeting, of whom about 60 were from the five participating institutions while the remainder were individuals and representatives of establishments having a research interest in the field of stress-corrosion cracking. About 35 papers and research progress reports were presented to the meeting during the three days; in addition to the particular discussions which followed many of the papers, two periods were set aside for general discussion. All the papers were presented by Program personnel, but the invited guests participated in and made very useful contributions to the discussions.

The general impression of this, the first of the annual review meetings, was that it provided a valuable forum for the presentation of both complete and incomplete research work, that it provided a useful exchange of ideas, and that it encouraged the establishment of personal contacts both inside and outside the Program.

A two-day symposium on the nature and properties of metallic surfaces as revealed by field ion microscopy will be held in conjunction with the 1968 Annual Meeting at Atlanta.

A two-day workshop was held at NRL on 22-23 June 1967. Fifteen faculty members and students from five universities observed a wide variety of fracture research experiments. Lectures related to the fracture problem were presented by Dr. G. R. Irwin, Professor A. A. Wells, Dr. E. P. Dahlberg, and Professor A. S. Tetelman.

During the summer of 1967, the following graduate students were in residence at NRL, either as employees of the Laboratory or of the Georgia Institute of Technology:

John Caron
Jim Hubbard
B. R. Livesay

Richard Margolis
David Mauney

Included in the students' activity for the summer was an environmental cracking problem from Viet Nam for which these students were asked to lay out a remedial program.

Mr. Ronald Livak spent the summer at The Boeing Company working with Jim Williams on structure of titanium alloys.

Dr. Piper of The Boeing Company is serving on special committees to provide recommended practices for the study of stress-corrosion cracking of titanium for both AGARD and ASTM G-1.

Dr. Anthony Kelly from the Metallurgy Department of the University of Cambridge in England participated in the ARPA Program at Carnegie-Mellon University this past quarter. Dr. Kelly has taught a formal course in "Strong Solids" and has introduced many of the students on the ARPA Program to current concepts of strength and fracture. He has also participated in innumerable discussions in the mechanical behavior of solids and in particular environmental effects on these properties. Dr. Kelly will be returning to England to take up the position of Superintendent of the Materials Division at the National Physical Laboratory. We certainly wish him well in his new position.

Professor A. A. Wells of Queen's University spent two weeks at NRL as a special consultant in the continuum mechanics of stress-corrosion crack propagation.

DOCUMENT CONTROL DATA - R & D

(Security classification of title body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) Naval Research Laboratory Washington, D.C. 20390		2a. REPORT SECURITY CLASSIFICATION Unclassified	
		2b. GROUP	
3. REPORT TITLE ARPA COUPLING PROGRAM ON STRESS-CORROSION CRACKING (Third Quarterly Report)			
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Quarterly Progress Report			
5. AUTHOR(S) (First name, middle initial, last name) Dahlberg, E.P. (General Editor)			
6. REPORT DATE August 1967		7a. TOTAL NO. OF PAGES 77	7b. NO. OF REFS 60
8a. CONTRACT OR GRANT NO. NRL Problems 61M04-08, 62M04-08 63M04-08A & 63M04-08B ARPA Order 878 & RR 007-08-44-5512		9a. ORIGINATOR'S REPORT NUMBER(S) NRL Memorandum Report 1812	
b. PROJECT NO.		9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
c.			
d.			
10. DISTRIBUTION STATEMENT This document has been approved for public release and sale; its distribution is unlimited.			
11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY Advanced Research Projects Agency of the Department of Defense and Office of Naval Research, Wash., D.C	
13. ABSTRACT <p>A progress report of the research investigations being carried out on the problem of stress-corrosion cracking of high strength materials under ARPA Order 878 is presented. Work at Carnegie-Mellon University, Lehigh University, Georgia Institute of Technology, The Boeing Company, and the Naval Research Laboratory concerning physical metallurgy, surface chemistry, fracture mechanics, and characterization tests and translation related to stress-corrosion cracking is described. The materials being studied include high strength steels, titanium alloys, and aluminum alloys. Abstracts of recently published reports and a diary of events are included.</p>			

14.

KEY WORDS

LINK A

LINK B

LINK C

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Stress-Corrosion Cracking
Titanium Alloys
Aluminum Alloys
High Strength Steels
Fracture Mechanics
Surface Chemistry
Salt Water Cracking